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*The*  
**TECHNOLOGY**  
*of*  
**ADHESIVES**

By

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*Technical Director, Plastics Industries Technical Institute  
Los Angeles, California*



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DEDICATED

*to*

*My Beloved Wife, Jill*



## FOREWORD

Developments in adhesives have closely paralleled developments in high polymers. For some unexplained reasons, adhesives have been deemed insignificant in comparison with the more colorful and utilitarian molded, laminated, and cast plastics. From a quantity production viewpoint, adhesives are not far removed from the figures for molded parts and surface coating materials. With growing interest in structural applications of plastics and the development of composite laminated structures of maximum efficiency, adhesives will assume a much more prominent position in the industrial picture.

In this volume I have endeavored to tie together as closely as possible developments in plastics with those in adhesives. To do this has meant giving considerable weight to the utilization of synthetic resins in adhesive formulations, in some instances disproportionate to the actual quantity used. However, it is hoped that these efforts will focus attention upon the latent possibilities of many compounds not fully explored.

There remain many gaps in the theories of adhesive action, though a brief survey of technical literature during the past few years will reveal that more attention is being given to that important subject. I have introduced new discussions which it is hoped will help to dispel the uncertainty and discordance surrounding adhesive phenomena.

To the Forest Products Laboratory and their frequent technical notes on wood technology and adhesives, I wish to make a grateful acknowledgment for permission to refer to some of their published data. Further, to numerous manufacturers and individuals who have furnished information helpful to the text, I express my appreciation. In the final assembling and preparation of the manuscript, I am grateful for the assistance of Mrs. Eve Lougee.

JOHN DELMONTE

*Glendale, California*  
*December, 1946*



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## Chapter 1

### Introduction and Classifications of Adhesives

Developments in adhesives have moved forward at an accelerating pace during the past ten years. This progress has been due in large measure to a greater selection of synthetic resins and rubbers and to a better understanding of the processes of polymerization. Since the start of World War II there has been an intensified effort to cope with the singular problems of high polymer adhesives. These efforts have laid the groundwork for which fundamental research and study will endeavor to find answers in the years to come.

In earlier years, most technical papers on adhesives dealt largely with the tabulation of various recipes, usually involving three or more components, with little or no discussion of the reasons why certain figures were arrived at, and very little quantitative data on the relative merits of various adhesives or their components. This early lack of quantitative data may be explained in part by the absence of standard testing methods and facilities, and failure to comprehend fully the very many variables which affect the performance of adhesives.

While the qualitative aspects of various adhesives may be predicted in part by knowledge of the chemical and physical nature of the materials, additional problems are introduced by the behavior of the materials as thin films rather than as solid masses. Further, the study of the adhesives must be made not upon a substance dissociated from other influences, but in relation to the surfaces of the materials being bonded, *i.e.*, their porosity, polar characteristics, occluded films, etc. No longer are we confronted solely with the bonding of cellulosic materials by various animal and vegetable glues: the field now embraces metals, ceramics, solid organic plastics, explosives, and rubbers.

To the chemist, physicist, and engineer the goals are tempting—new and revolutionary fabrication processes to replace screws, rivets, and high-temperature metal welding. In addition to attachment processes, many of the materials will be found capable of fulfilling the dual role of impregnation and adhesion with beneficial results. It is mathematically recognized that the assembly of machine or product components achieves the optimum in effectiveness when the stress distribution is substantially uniform throughout the length and breadth of the mating surfaces. The ideal adhesive achieves this condition when the transmission of stress from one element to another is obtained without discontinuity of stress

distribution along the surfaces to be joined. While physical aspects are quite significant, the development of these ideal adhesives is largely a chemical problem, depending on the nature of surfaces being bonded, though it appears unlikely that any one adhesive will have universal adaptability to all surfaces.

The optimum in adhesives is of course, the attainment of a bonding strength at least equal, if not superior to the pertinent physical properties of the materials being bonded. A less severe, though more practical premise, is that the adhesive should be functionally acceptable throughout the life and environmental influences of its application.

### Basic Definitions

An adhesive substance has long been considered as a material capable of adhering or sticking to a surface, primarily to promote a bond between that surface and another material. Before the wide-scale utilization of synthetic resins, the terms "adhesive" and "glue" were considered synonymous because the earliest commercial adhesives were glues, and were generally of animal or marine origin. The term "glue" is still widely used, and such expressions as "glue line", "glue pot", and "glue spreader" find prominent places in our vocabulary, even though they do not necessarily refer to animal glue. The term "glue" generally implies a substance of a sticky character, while many of the modern adhesives are not sticky or tacky in application. An adhesive, however, is a more inclusive expression, encompassing many types of synthetic resins, cellulosic resins, natural resins, and the glues of animal origin.

Neither does the ability of a material to produce a bond between two substances stamp it as an adhesive, because such bonds may be very temporary in character. For example, water, butter, paraffin wax, and many other common substances can produce bonds upon solidification. Of course, many pure organic substances are yielding valuable information on the surface chemistry of materials and hence are contributing to the development of adequate theories of adhesion, though for practical purposes the definition of an adhesive should be predicated upon the work it is to accomplish. With these qualifications, it is now possible to offer the following definition:

*Organic Adhesive:* An organic material capable of producing a substantially permanent union between two or more materials. This definition also recognizes temporary pressure-sensitive adhesives, which are capable of substantially permanent adhesion if required. It does, however, eliminate a number of organic liquids whose sole claim to adhesiveness is high viscosity and low cohesion.

Organic adhesives may in turn be classified in accordance with the sub-

stances from which they are prepared, such as synthetic resin adhesives; synthetic resin-rubber adhesives; rubber and synthetic rubber adhesives; protein adhesives; adhesives of animal and fish origin; adhesives of vegetable origin; cellulosic derivative adhesives; and various inorganic-organic adhesive combinations. Throughout this book emphasis will be placed upon the synthetic resin adhesives and their combinations with other materials, such as rubbers, proteins, cellulose, etc. It is highly desirable also to correlate studies based upon inorganic adhesives, such as sodium silicates, and those of protein, animal, and vegetable origin with the present analysis, because much can be learned from the technology of established adhesives which have enjoyed and are still enjoying many successful applications.

When an effort is made to classify adhesives according to their chemical constitution, it becomes increasingly evident that the developments in organic adhesives closely parallel those in organic plastics. As the research chemist develops new synthetic resins and new cellulose derivatives, or finds new ways of obtaining or processing natural or synthetic resins, he endeavors to translate his discoveries into practical usefulness. The great majority of plastics materials have been proposed at one time or other as adhesives, though only few have been pre-eminent in this respect; the others have found success in the more voluminous fields of molding, laminating, casting, and surface coatings. The time is not distant, however, when adhesives will be formulated on the basis of chemical and physical structure, rather than the cut and try experimentation of earlier days.

### Historical Background of Adhesives

The history of adhesives up to the present century is largely the history of animal glues and their applications. The romance of the art of gluing has been vividly portrayed by Darrow<sup>1</sup>, who reviews Egyptian, Roman, Renaissance, and more modern references in the application of glues, culminating in the development of vegetable adhesives from cassava flour. While Egyptian murals and veneered caskets in our museums indicate the early origin of the art of gluing, we can assume that the Egyptians, who acquired so many of their arts from earlier races, simply carried on and applied the knowledge whose origin is lost in the shadows of history.

The first commercial glue plant was founded in Holland in 1690, and the first glue factory in the United States in 1808 by Elijah Upton, founder of the American Glue Company of Boston. It is a noteworthy fact that up to this century the great majority of glue applications were in the manufacture of furniture, and in the review of books on the art of furniture manufacture, mention of the use of glues often occurs. Not all early glues were of animal origin, because there are early English references to glues

prepared from fish offal.<sup>2</sup> England began manufacturing glue and established it as a permanent industry around 1700. In the United States the first patent literature on the production of glues from animal bones appeared in 1814. The history of modern adhesives really begins with the start of the twentieth century, because the art prior to that time was little changed from the technique known to the Egyptians.

Table 1. Chronological Developments of Adhesives in United States.

Year	Material
1814	Glue from Animal Bones (Patent)
1872	Domestic Manufacture of Fish Glues (Isinglass)
1874	First U. S. Fish Glue Patent
1875	Laminating of Thin Wood Veneers Attains Commercial Importance
1909	Vegetable Adhesives from Cassava Flour (F. G. Perkins)
1912	Phenolic Resin to Plywood (Bakeland-Thurlow)
1915	Blood Albumen in Adhesives for Wood (Haskelite Co.)
1917	Casein Glues for Aircraft Construction
1920-30	Developments in Cellulose Ester Adhesives and Alkyd Resin Adhesives
1927	Cyclized Rubber in Adhesives (Fischer-Goodrich Co.)
1928	Chloroprene Adhesives (McDonald-B. B. Chemical Co.)
1928-30	Soybean Adhesives (I. F. Laucks Co.)
1930	Urea-formaldehyde Resin Adhesives
1930-35	Specialty Pressure-Sensitive Tapes: Rubber Base (Drew-Minnesota Mining & Mfg. Co.)
1935	Phenolic Resin Adhesive Films (Resinous Products & Chemical Co.)
1939	Polyvinyl Acetate Adhesives (Carbide & Carbon Chemicals Co.)
1940	Chlorinated Rubber Adhesives
1941	Melamine-formaldehyde Resin Adhesives (American Cyanamid Corp.) and "Redux" by de Bruyne (Aero Research Ltd.)
1942	"Cycleweld" Metal Adhesives (Saunders-Chrysler Corp.)
1943	Resorcinol-formaldehyde Adhesives (Penn. Coal Products Co.)
1944	"Metlbond" Adhesives (Havens, Consolidated Vultee-Aircraft Corp.)
1945	Furane Resin Adhesives (Delmonte, Plastics Inst.) and "Pliobond" (Goodyear Tire & Rubber Co.)

It is not an easy matter to prepare a chronological interpretation of the recent developments in modern organic adhesives, because in most cases the chemical developments antedate the attainment of commercial importance by a number of years. However, in the foregoing table are noted some of the outstanding adhesive developments or trends in the United States. The developments are tabulated according to their first public disclosures, whether by patent or citations in technical literature.

The preceding list is by no means complete, the large number of patents

issued on adhesives each year testifying to the transient character of many of these developments. However, the list is significant in that it denotes the trend toward the synthetic resin developments. Chronological developments in the field of organic plastics run parallel to the appearance of adhesives. In the individual chapters on various adhesives, more attention will be given to other adhesive developments in this country and abroad, which are not indicated on the above list.

Also of fundamental importance to the field of adhesives are certain equipment developments, primarily for generating heat and expediting the cure of the resin. High-frequency heating of glue lines, first put into wide commercial practice in 1943, promises to extend greatly the fields of applications of adhesives by permitting thick bonded sections to develop full strength in a short time.

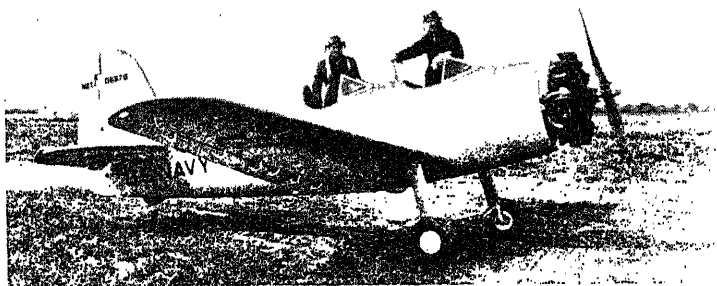


Figure 1. Training plane manufactured from resin bonded plywood during World War II. (Courtesy Timm Aircraft Co.)

The trend in synthetic resin adhesives may also be followed by observing their applications. Prior to the twentieth century the bonding of wood veneers and the assembly of furniture employed large quantities of adhesives. The sealing of envelopes, book-binding, and other paper and cloth applications established further markets for the materials. Synthetic resin adhesives for corrugated paper-board manufacture and pressure-sensitive tapes are more recent. World War II brought out a number of new large-scale applications to boat, aircraft and building construction. Laminated keels for small boats; laminated wood spars for aircraft; resin-bonded plywood monocoque constructions for wings and fuselages; drop-pable fuel tanks; and innumerable aircraft assemblies found satisfactory production materials and methods in synthetic resin adhesives and bag molding techniques. Figure 1 shows one of the early synthetic-resin bonded plywood aircraft training airplanes produced during 1942.

Of permanent significance are the trends in adhesive developments in

the building trade. Large laminated glued arches have been prepared, some with a span of close to 100 feet<sup>3, 4</sup>. Synthetic-resin adhesives are now beginning to be recognized in building codes, which encourage the proper and controlled applications to structural design<sup>5</sup>.

Aside from the wood field, resin and rubber adhesives for metals show much promise<sup>6, 7, 8, 9</sup>. The uniting of aluminum alloys and the joining of steel with joint shear strengths of 3000 psi were unheard of a few years ago; this figure is now readily attained by several adhesives. The entire subject of metal bonding abounds with such latent possibilities that a much more complete discussion is reserved for a later chapter. Ceramics, glass, textiles, rubbers, and solid organic plastics are now being bonded with adhesives which form glue lines stronger than the materials themselves. The processes of fabrication and assembly are being revised to permit such assemblies. Trends in modern adhesives are also reflected in applications involving widely dissimilar materials. To illustrate a few examples at random: Rubber O-rings to metal valves; rubber sealing strips on polymethyl methacrylate canopies; composite laminates of glass cloth to wood; non-porous adhesive assemblies of sewer pipes; and infinite other combinations.

Not only have modern adhesives greatly extended the fields of plastics and rubber-like products, but they have also inspired confidence among engineers and designers in their permanence of quality. The permanence is apparent under severe temperature and humidity changes and in atmospheres conducive to fungi growth—conditions extremely detrimental to the earlier animal and vegetable adhesives.

### Production Estimates for Various Adhesives

Reliable figures for the production and distribution of synthetic-resin adhesives during recent years are very meager, first because of the relative newness of the materials and second because of war secrecy understandings. However, there are reliable data on animal, vegetable, casein, and fish glue production up to 1938. Various figures compiled by the U. S. Tariff Commission are reported in Table 2<sup>10</sup>.

In 1939 there were twenty major producers of animal glues in this country, a number of them manufacturing glue as a by-product of meat packing or rendering of animal fat. Others, concentrating on hide or extracted bones, engaged solely in glue manufacture. In 1935 there were about 25 domestic producers of vegetable glues, about one-half of the production being from cassava (tapioca) flour. Cornstarch and soybean cake meals were the other major sources of raw materials. In 1938 there were at least seventeen companies producing casein glues, though a substantial concentration was in the hands of four producers. The demands

of the paper industry accounted for over 85 per cent of casein glues in 1935, largely as sizing for coated paper, producing bonds to the clay coating. Among the fish glues, three companies account for over three-quarters of the entire production.

Table 2. Adhesive Production in United States (Millions of Pounds).

Year	Animal Glues (all kinds)	Vegetable Glues*	Casein Glues	Fish Glues
1924	99.6			4.9
1925	97.1			4.98
1926	100.1			5.07
1927	112.3	97.1	3.2	4.99
1928	103.6			4.97
1929	106.4	133.1	6.76	5.26
1930	103.1			5.13
1931	89.4	102.5	4.78	4.22
1932	61.7			3.56
1933	49.9			3.47
1934				3.89
1935	87.0	126.8	5.87	3.99
1936	110.1			4.22
1937	121.6	230.0	7.98	4.31
1938	87.8	165.6	7.27	3.74

\* Includes figures for soybean protein adhesives.

Average prices for the representative glues discussed in the preceding paragraphs are as follows:

Hide and extracted bone glues	0.15 cents per pound
Vegetable glues	.10 " " "
Casein glues	.13 " " "
Fish glues	.21 " " "

As pointed out before, the actual trend in synthetic-resin adhesives during World War II has been cloaked in military secrecy, though since Sept. 1943, the War Production Board has issued monthly figures on essential civilian end uses. These do not include military uses, however. To quote a few representative figures<sup>11, 12</sup>:

When Allocated	Material	Amount (Pounds)
For 2d Quarter, 1944	Phenol-formaldehyde Adhesives	762,000—Adhesives
		2,511,000—Abrasives
		2,859,000—Asbestos
		(Brake linings, clutch facings)
Total for 1943 (U. S.)	Urea-formaldehyde Adhesives	32,546,000
Total for 1943 (U. S.)	Phenol-formaldehyde Adhesives	10,290,000

Table 3. Chemical Classifications of Adhesives and Typical End Uses

*Thermosetting Synthetic Resin Adhesives:*

Phenol-formaldehyde	Woods, cloths, paper, miscellaneous
Phenol-furfuraldehyde	Woods, cloths, paper, miscellaneous
Resorcinol-formaldehyde	Woods, plastics, rubbers
Urea-formaldehyde	Woods, textiles
Melamine formaldehyde	Woods, textiles
Furanes	Plastics, rubbers, miscellaneous
Polyester Resins (incl. alkyds and allyls)	Cloth, glass fabrics, insulation
Aniline formaldehyde	Woods, plastics
Polyurethanes	Woods, miscellaneous

*Thermoplastic Synthetic Resin Adhesives:*

Polyisobutylene	Tapes, foils, miscellaneous
Polyvinyl acetate	Metals, paper, miscellaneous
Polyvinyl chloride-acetate	Miscellaneous
Polyamides	Metals, woods, miscellaneous
Silicones	Insulating materials
Polymethacrylic and polyacrylic esters	Safety glass, miscellaneous
Coumarone-indenes	Rubber, plasticizer
Polyvinyl butyral	Safety glass, miscellaneous
<i>p</i> -Toluenesulphonamide-aldehydes	Safety glass, plasticizer
Polystyrene	Shoe cements
Maleic anhydride adducts-glycerol-fatty acid resins	Plasticizers, miscellaneous
Polyvinyl ethers	Paper, wood, miscellaneous

*Cellulosic and Starch Derivatives:*

Cellulose nitrate	Leather, paper, miscellaneous
Cellulose acetate	Leather, paper, miscellaneous
Ethylcellulose	Paper, cloth, miscellaneous
Methylcellulose	Paper, modifier, thickener
Sodium carboxymethyl cellulose	Thickener, paper
Starch, Dextrin	Paper, wood, textiles

*Natural Resins and Oils in Adhesives:*

Rosin and rosin esters	Plasticizers and modifiers
Shellac	Insulation, miscellaneous
Asphalts	Minerals, miscellaneous
Gum tragacanth	Thickener for proteins, starch
Ester gum	Plasticizer and modifier
Linseed oil (oxidized)	Linoleum, miscellaneous
Sulphite waste liquors	Linoleum

*Water-soluble Gums in Adhesives:*

Gum arabic	Postage, paper, miscellaneous
Gum senegal	Paper, miscellaneous
Cerasin gum	Mixtures with arabic

Table 3—*Concluded**Protein adhesives:*

Casein	Wood, paper, miscellaneous
Soybean protein	Plywood
Zein	Paper, miscellaneous

*Adhesives of Animal or Fish Origin:*

Glue (hide, extracted bone, green bone)	Wood, tapes, miscellaneous
Fish offal	Wood, miscellaneous
Blood albumen	Modifiers for synthetic resin and cellulosic adhesives and proteins

*Adhesives from Rubber or Synthetic Rubber:*

Rubber latex	Cloth, paper, miscellaneous
Natural or reclaimed rubber	Rubber, metal, miscellaneous
Chlorinated rubber and rubber hydrochloride	Miscellaneous, rubber, metals
Cyclized rubber	Miscellaneous, rubber, metals, paper
Polychloroprene	Leather, miscellaneous
Butadiene-acrylo-nitrile copolymer	Paper, metals, miscellaneous
Synthetic resin-rubber combinations	Metals, plastics, miscellaneous
Chlorinated synthetic rubbers	Miscellaneous

*Inorganic Adhesives:*

Sodium silicate	Corrugated paper, paper products
Portland cement	Mineral aggregates
Magnesium oxychloride	Ceramics
Plaster of paris	Miscellaneous, ceramics
Litharge-glycerin	Ceramics, plumbing

More recent statistics published by the Dept. of Commerce since the stop of the war reveal that during 1946 the monthly production of phenolic adhesives averages at 1,100,000 pounds and that urea and melamine adhesives are about 3,000,000 pounds<sup>12</sup>.

**Chemical Classifications of Adhesives**

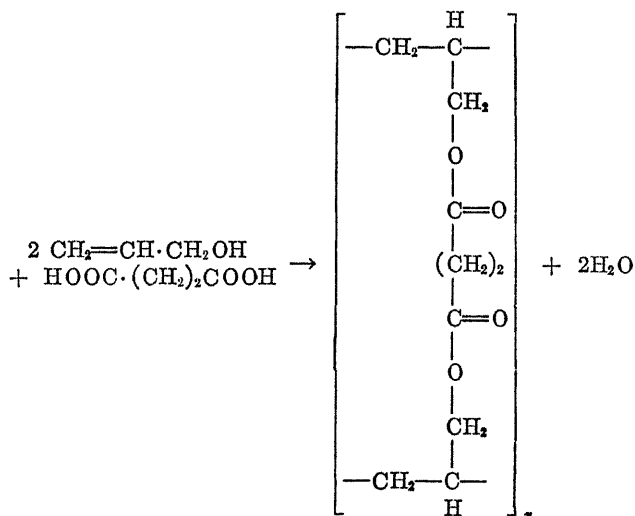
The most widely used method of classifying adhesives is in accordance with their origin or the materials employed in their manufacture. When two or more high polymers are used, the major component should designate the chemical classification. One recent publication suggests adhesives from animal origin (animal glue, fish glue, and casein); adhesives of vegetable origin (starch, cellulose derivatives, rubber, and gum exudations); and synthetics (phenolics, vinyls, and urea formaldehyde)<sup>13</sup>. However, if chemical classifications are to be employed, a much more comprehensive

tabulation would assist further analyses of the problems of adhesion. Table 3 carries this out to some extent.

The chemical classifications for adhesives appearing in Table 3 emphasize the tremendous advance made in this field in recent years. Various members of these groups are the subject of further study in subsequent chapters. In many instances it will be found that combinations of materials rather than any single entity will provide the basis of an adhesive formulation.

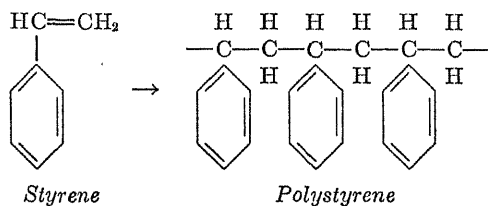
**Thermosetting synthetic resin adhesives**, through the action of heat, catalysts, or both may be converted to a substantially infusible and insoluble state. This conversion is marked by a growth to an indeterminately high molecular weight, punctuated by cross-linking between the molecular chains. The thermosetting resins may be formed by condensation-polymerization reactions, such as phenol-aldehydes or urea-aldehydes; by the presence of two or more groups, each capable of additional polymerization, such as divinyl benzene or diallyl succinate; by the presence of trifunctional and difunctional molecules, such as glyceryl-succinate; or combinations of the preceding mechanisms.

Many useful resins are prepared from compounds which possess a number of reactive groups. A functional group in the monomer is that portion of the molecule which contributes to a reaction step. Such groups are, *e.g.*, OH, NH<sub>2</sub>, COOH, SO<sub>3</sub>H, etc. Accordingly, if the monomer contains one, two, three, or more, it is called monofunctional, bifunctional, trifunctional or polyfunctional<sup>14</sup>. It is apparent that the presence of trifunctional molecules with bifunctional materials will result in cross-linked polymers, as in the case of diallyl succinate:



While water may be formed as a by-product in condensation-polymerization reactions during the formation of phenolic, urea, or alkyd resins, the formation of a thermosetting structure may take place without water as a by-product. Many examples of polyester resins illustrate this point. Tri- or polyfunctionality is necessary, however, for forming a thermosetting polymer. On the other hand, bifunctional molecules form linear thermoplastic materials.

**Thermoplastic synthetic resin adhesives** are characterized by permanent fusibility and solubility. They will soften with heat and exhibit a greater degree of creep under sustained stress. Thermoplastic resins may be formed by a simple addition polymerization where the starting molecule, called the monomer, joins to itself to form a dimer, then a trimer, etc., to many molecules or polymer. Many hundreds of monomeric units may be linked together to form the polymer, as for example, when styrene polymerizes to polystyrene:



Thermoplastic resins are also formed through interaction of bifunctional molecules, such as  $x-R-x$ ,  $x-R-y$ ,  $-x-R'-x$ , and  $x-R'-y$ , where  $-R'-$  and  $-R-$  represent bivalent radicals, and  $x$  and  $y$  functional groups ( $NH_2$ ,  $OH$ ,  $COOH$ , etc.) capable of reacting with each other to form a new functional group, generally with the elimination of a simple by-product, as  $HOH$ ,  $HCl$ ,  $NH_3$ . As Carothers points out<sup>14</sup>, if the bifunctional reactions lead to larger than six-membered rings, a high molecular weight polymer will form.

Polymerization has usually been completed before the thermoplastic resin is applied as an adhesive, and then usually in combination with solvents and various modifying agents. The solvent serves simply as a vehicle for distributing the resins more effectively, and the development of adhesion proceeds as the solvent evaporates. In many instances their thermoplasticity will permit heat softening and heat welding.

As will be discussed more fully later, it is quite important in studying the fundamental properties of synthetic resins in relation to the theories of adhesion that particular attention be given to the nature of the side groups which influence the chemical properties of the materials as well as their polar characteristics. Certain side groups in polymer chains have a much greater tendency to establish forces between chains than others, and the

effect of these forces may be considerable<sup>15</sup>. Molecular weight distribution curves will warrant examination in determining the adhesive qualities of high polymers not only because of their influence on the solvent concentration-viscosity relationships, but also because the adhesive and cohesive forces of the resin will vary with the degree of polymerization.

**Naturally occurring polymers**, such as cellulose, rubber, starch, and proteins, formed the chief basis of adhesives before the development of synthetic resins. Considering these materials as other forms of high polymers will reveal much useful information which will guide the developments in synthetic resin adhesives. In a number of instances which will be cited later excellent combinations have been prepared with synthetic resins and natural high polymers. These combinations are often made possible by a third component in which both are mutually compatible. It is reasonable to suppose that in the cementing of dissimilar surfaces the ideal adhesive would be comprised of components having a particular affinity for each of the surfaces to be mated.

Many data have been obtained on the effect of plasticizers and the influence of side groupings in the adaptation of naturally occurring high polymers to adhesive problems. For example, cellulose esters of heterogeneously linked dicarboxylic acids, such as cellulose acetate glycollate, etc., are marked by superior adhesive properties<sup>16, 17</sup>. Likewise, cyclization of rubber proved to be the basis of a number of industrially important adhesives<sup>18</sup>. In these and numerous other examples the fundamental basis for successful adhesives will be found. These fundamentals will be reviewed in a subsequent chapter on the theory of adhesion.

There are other ways of classifying adhesives besides identification of their origin, or their thermosetting or thermoplastic qualities. One excellent method depends upon the manner in which the adhesive sets or gels. Browne<sup>19</sup> has suggested the following groupings: (1) glues that gel by cooling of lyophilic sols; (2) glues that gel by heating of lyophilic sols (blood albumin); (3) glues that gel without temperature change as a result of chemical reaction; (4) glues that gel through solvent evaporation; and (5) glues in which gelation is brought on by heat without use of a solvent. The adhesive may fall into more than one of the above classifications. For example, polyvinyl acetate adhesives may be formulated to be welded by heat in the absence of solvents, or they may be dissolved in a volatile solvent and be applied in the liquid state.

In considering a method of classifying adhesives by their setting or gelling properties it is important to define what is meant by *set* or by *gel*. A liquid sol is considered to have gelled when the dispersed phase forms a coherent network, which is still saturated with the liquid dispersing medium. The disappearance of the liquid dispersing medium, either through

evaporation or by diffusion into a porous body, contributes to improved strength in the adhesive material, and when functionally acceptable the adhesive is considered to be *set*. Of course thixotropy will introduce other complications in defining gels, though in the formation of most adhesives the attainment of a gel proceeds quite rapidly. Gemant has reviewed the difference between gels and sols through consideration of the potential levels<sup>20</sup>.

Transformations from liquid to gelled states take place quite rapidly for thermosetting synthetic-resin adhesives under the proper conditions. Thixotropic effects are not evident in these instances due to the intermolecular cross-linking between polymers. The viscosity-concentration relationships of high polymer-solvent combinations used as adhesives show a rapid approach to the gelled state, as the solvent is lost by evaporation or diffusion<sup>22, 23</sup>. Likewise, aqueous emulsions of high molecular weight polymers will show a rapid viscosity increase to a stiff consistency simulating the gelled state after passing a certain per cent solids range. This rapid change in viscosity has for example, many practical advantages in the application of sodium silicate adhesives to the manufacture of corrugated fiber-board.<sup>21</sup> Other thermoplastics will behave in a similar manner.

There is one further instance of gelling which should be considered, and that is gel formation in solution upon the addition of reagents which promote cross-linking between high molecular weight chains or insolubilize the polymers present. For example, it is well known that aldehydes, while increasing the water resistance of protein glues, will also decrease stability<sup>24</sup>. A small amount of divinyl benzene will insolubilize or gel polystyrene<sup>25</sup>.

Consequently, it is now suggested that Table 4 serve as a method of classifying adhesives according to their gel forming characteristics:

Table 4. Classification of Adhesives According to Their Method of Forming Gels.

- 
- |   |
|---|
| 1. Gel formation by Loss of Volatile Constituent by Evaporation or Diffusion    |
| a. Loss of Organic Solvent: Polyvinyl acetate or rubber solution                |
| b. Loss of Water: Starch, animal glues, rubber latex, sodium silicate, etc.     |
| 2. Gel Formation by Condensation-Polymerization, Induced by Heat and Catalysts: |
| Urea-formaldehyde, melamine-formaldehyde and phenol-formaldehyde                |
| 3. Gel Formation by Polymerization, Induced by Heat, Catalysts, and/or Light:   |
| Various polyesters and allyl resins   |
- 

Less exact, though more simple methods of classifying various adhesives have been suggested on the basis of solvent or non-solvent properties, and hot or cold setting<sup>26</sup>. As a matter of fact, the most widely used practical method of classifying adhesives is based on their temperature characteris-

tics. While the selection of the temperature ranges is entirely empirical, the following tabulation indicates the distinctions usually made:

- (1) Hot-setting adhesives: 220° F and higher
- (2) Warm-setting adhesives: 140° to 220° F
- (3) Cold or room-temperature setting adhesive: 75° to 140° F

The higher temperatures may: (a) decrease viscosities of solutions so that on cooling a gel will form, as in setting certain animal glues; (b) hasten the evaporation of solvent and hence the development of tackiness and gel formation in a thermoplastic synthetic-resin adhesive; (c) expedite polymerization of the thermosetting synthetic-resin adhesive; or (d) soften the solventless thermoplastic to permit heat welding.

There are a number of additional factors which must be considered in applying heat to hasten the setting of the adhesive. These factors are related to the more practical aspects of production gluing. Thermosetting-resin adhesives which are set by heat generally undergo a conversion from a fusible, soluble state to an infusible, insoluble state through a multiplicity of intermolecular combinations. The temperature may either increase the rate of resinification or else activate a catalyst normally latent at room temperature. As an example of this art in setting urea-aldehyde resins, Howald employs B-Bromhydrocinnamic acid or isodibrom succinic anhydride which liberates hydrogen bromide<sup>28</sup>.

During the conversion period the resin adhesive may acquire high mobility, and may disappear from its vantage point at the glue line by diffusion into a porous surface or by sweating out at the ends. The resin adhesive manufacturer may advance the stage of resinification sufficiently to prevent excess fluidity, or else introduce an inert filler which will retain the adhesive more readily. This increase in flowability with a rise in temperature has, as a matter of fact, been employed as a technique of impregnating plywood veneers at the time of bonding<sup>27</sup>. The extent of penetration into the wood was observed to depend upon the molecular weight of the bonding resin.

The application of heat to thermoplastic synthetic resins is generally for an entirely different purpose than above. Polymerization of the resin has already been substantially effected before it has been compounded into an adhesive, though the function of the heat is to soften the resin sufficiently to permit heat sealing. Heat sealing of packages or containers is practiced on a wide scale. Various organic plastics, in the form of thin foils or films deposited upon other surfaces are exposed to a high temperature for a short interval of time, generally accompanied by pressure, which must be maintained during at least a portion of the cooling period. Among materials which may be effectively bonded in this manner are ethyl-

cellulose, polyvinyl acetate, rubber hydrochloride, and others. A strong permanent bond may be readily achieved, which has a strength unattainable by other methods. The temperature of heat sealing is a function of the material to be heat sealed and the time available for developing adequate adhesion. The time element may even be a fraction of one second on automatic equipment. Not to be overlooked is the effect of temperature upon the materials being bonded. Cellulosic materials in particular experience decided moisture gradients which will produce internal stresses.

Warm-setting adhesives bridge the gap between high-temperature setting types and the room or low-temperature setting materials. Representative members of this group include melamine-urea-formaldehyde resin adhesives and some phenol-resorcinol-formaldehyde resins. As a group, a compromise is reached between the catalysts of low-temperature setting types and the benefits of heat activation. They are generally selected for applications with somewhat limited heating facilities.

Much popular interest has always been evinced in low or room-temperature setting adhesives. While the production advantages of hot-gluing methods have long been recognized<sup>29, 30, 31, 32</sup>, many small fabricators are not equipped for controlled high-temperature gluing. Animal glues, adhesives from natural gums, starch and dextrin, and various proteins have been and will continue to be popular for the low-cost, room-temperature setting applications they have fostered<sup>33</sup>. Cold-setting properties are obtained by catalysis of thermosetting synthetic resins with acids or alkalies; by withholding the resin-forming ingredients until resinification is desired; or by removing volatiles from solutions or emulsions of high polymers. Catalysts introduce additional problems in their probable effect upon the materials being bonded, necessitating for example, a lower pH limit of 2.5 on adhesives for aircraft plywood<sup>34</sup>.

### Solvent Effects on Adhesives

No discussion of the classifications of adhesives is complete without some examination of the effect of solvents on adhesives. Broadly, adhesives may be classified as solvent and non-solvent types, though the latter are relatively few, and are limited largely to liquid, heat-convertible thermosetting synthetic resins or thermoplastic adhesives designed to be heat sealed. The solvent, whether water or an organic liquid, may play a significant role in the development of adhesion, or else its retention by the resin at the glue line may influence the setting, and the subsequent ability of the adhesive to resist creep and cold flow. Further, the characteristics of the resin films formed on the evaporation of solvents have been shown to be dependent upon the nature of the solvent or solvent combination<sup>35</sup>.

The expression "solvent cement" is frequently heard in connection with

the bonding of thermoplastic synthetic resins. Various solvents, such as acetone for the cellulose derivatives, are employed to wet the surfaces to be bonded, and when the surfaces are in a soft, tacky condition they are pressed firmly together. As a matter of fact, many of the proprietary cements for thermoplastics are based upon solvent or solvent combination, plasticizer, and a solution of the polymer itself. For example, patent literature abounds with solutions of "Celluloid" scrap and plasticizers as adhesive agents<sup>36, 37, 38, 39</sup>.

There are many advantages to handling adhesives in liquid form, because they will then permit application from glue-spreading rolls or spraying in position—techniques which are important to the covering of large surfaces. Thus, for example, a partially polymerized phenol-formaldehyde resin dissolved in alcohol forms the basis for a phenolic resin varnish—in this case a solvent-type adhesive. Similarly, polyvinyl acetate in methyl acetate, sodium silicate in water, and casein in alkaline solutions, are other examples of solvent-type adhesives.

The selection of the solvent, or in most cases, solvent combinations, depends upon several important factors. In most cases solutions of synthetic-resin adhesives are formulated to obtain maximum solids content with minimum solution viscosity. The inclusion of partial solvents with true solvents may effect some lowering of viscosity and hence potential increase of solids content. The selection of high polymers is usually based on their average molecular weight, consistent with the physical qualities desired at the glue line. Staudinger's viscosity relationship<sup>40</sup> expresses the relationship between solution viscosity and molecular weight:

$$V_{sp}/C = K_M \cdot M$$

for solutions of low concentration.  $K_M$  is the constant for the particular polymer in the solvent used,  $c$  is the concentration of the basic polymeric structural unit in moles per liter, and  $M$  is the molecular weight. The specific viscosity,  $V_{sp}$ , is obtained from:

$$V_{sp} = V_{rel.} - 1$$

where the relative viscosity,  $V_{rel.}$ , is the ratio of the viscosity of the solution to that of the pure solvent. Thus the specific viscosity is proportional to the molecular weight for low molecular weights, while at higher concentrations the relative viscosity varies widely with solvent employed. Typical values of Staudinger's constants are given in Table 5<sup>41</sup>.

In their effect upon solid organic plastics, organic liquids may be classified as: solvents, which effect complete dissolution of the material; non-solvents, which have no effect; and partial solvents, which may lower the strength without dissolving the material. A quantitative study has been

made of the effect of various solvents upon solid organic plastics by observing changes in the physical properties as a function of the time of contact with the solvent<sup>42</sup>. These same data indicate the comparatively rapid rate with which solvents penetrate into thermoplastic synthetic resins, as for example, Figure 2, illustrating a true solvent and partial solvent for polymethyl methacrylate. The retention of such solvents at the glue line will result in a serious loss of strength.

Table 5. Typical Staudinger Constants

Polymer	Solvent	$K_m \times 10^{-4}$
Polystyrene	Toluene	1.8
Polyvinyl acetate	Benzene	2.6
Ethylcellulose	$\text{CH}_2\text{Cl}_2$	12.5
Alkyl methacrylates	Benzene	1.7
Cellulose acetate	Acetone	10.25
Cellulose nitrate	Acetone	11.00

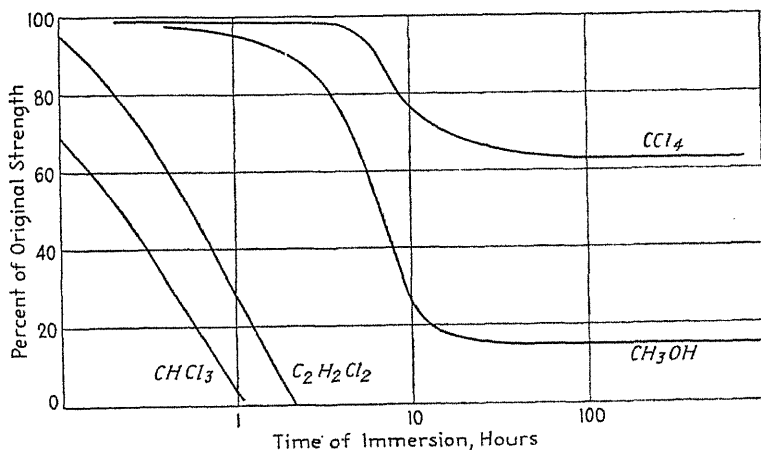


Figure 2. Effect of two true solvents and two partial solvents on acrylic polymers

In the formulation of adhesives the presence of solvents may inhibit the rate of gelation, particularly for thermosetting resins or adhesives formulated from rubbers and synthetic rubbers. This of course would be another desirable reason for the inclusion of solvents in adhesive formulations, though their complete elimination after application is necessary for best properties in the final bonded state.

The effectiveness of a solvent cement depends upon the average molecular weight of the polymer, and the nature of the side chains. For example, the effect of solvents upon cellulose derivatives is well known to be de-

pendent upon the degree of esterification or etherification<sup>43</sup>. Likewise, the increased molecular weight and higher chloride content of polyvinyl chloride acetate polymers have a decided bearing upon their solvation characteristics.

From the viewpoint of a gap-filling adhesive, non-solvent types have a great advantage over solvent-type adhesives. Having no volatiles to evaporate, the non-solvent type of adhesive may be literally cast into large voids and contribute to the mechanical soundness of the joint. Liquid furane resin adhesives and polyesters exhibit these qualities to a satisfactory degree. The evaporation of volatiles from solvent-type adhesives leaves fissures or discontinuities in the large gaps, lessening the strength appreciably. Some of the high solids content and high-viscosity thermosetting synthetic-resin adhesives of phenol furfural or resorcinol formaldehyde with adequate fillers (solids usually around 70 to 75 per cent) are nevertheless better as gap-filling cements than a thermoplastic synthetic-resin adhesive with say 20 to 35 per cent solids content.

### Physical Classifications of Adhesives

The physical state of the adhesive generally determines how it is going to be applied, and therein lies a practical basis for classifying adhesives. Many applications require the adhesive to be in a *liquid state* which lends itself to ease of spreading. In production this means mechanical glue spreaders for flat stock or sprayed or brushed applications to curved or irregularly shaped surfaces.

Besides the liquid adhesives, there are *pastes* and *foams*. The pastes may be softened by warming or extruded under small pressure upon the surfaces to be bonded. The high viscosities of the pastes allow them to be used on vertical surfaces with little danger of flowing off before assembly, and permit greater glue line thicknesses for certain applications. Some of the more stable pastes are conveniently packaged in collapsible tubes from which they are squeezed out.

Foam adhesives<sup>44, 45</sup> are of more recent origin, developed largely for the requirements of the wood industry. One objection to applying low-viscosity adhesives to porous surfaces is that this leaves a "starved" glue line with insufficient adhesive for good bonding. The inclusion of air or gas bubbles within the adhesive, as in the manufacture of the foam type, permits a broader distribution of the adhesive, with less tendency to leave a starved glue line.

Other physical forms in which adhesives are applied include tapes and films. Pressure-sensitive masking and sealing tapes for industrial and medicinal purposes are very well known, and enjoy a large market in this country. Rubber adhesive faces predominate in such tapes, though con-

siderable work has been done to prevent the adhesive from sticking to itself during wrapping or from permanently adhering to other surfaces<sup>46, 47, 48</sup>. Adhesive films may comprise a thin cast or calendered sheet of the adhesive, or else a layer deposited upon or impregnated into a thin sheet of cloth or tissue paper. Phenolic resin film has long been employed in the manufacture of hot-pressed plywood<sup>49</sup>. Gummed labels or envelopes would be classified as thin film applications of adhesives. These are activated for adhesion by remoistening with water or solvent.

One further form which warrants physical classification is the *powdered* or granular adhesive used in this state. The powder is spread at the glue line and depends upon heat and pressure to produce flow and uniform distribution. One interesting metal-bonding agent is applied in this manner<sup>50</sup>, though powdered adhesives are rather the exception than the rule.

Hence it is possible to classify adhesives according to their physical states in the following manner:

- (1) Adhesives in liquid form;
- (2) Adhesive pastes;
- (3) Adhesive foams;
- (4) Films of resin adhesives
  - (a) Pure
  - (b) Deposited on backing strip
- (5) Pressure-sensitive adhesive tapes;
- (6) Adhesive powders.

### Miscellaneous Methods of Classifying Adhesives

In the practical applications of adhesives there are non-technical methods of classifying adhesives according to their end use. For example, the expressions "primary bonding" and "secondary bonding" are well known to the many manufacturers of aircraft sub-assemblies. These terms may be defined as follows:

*Primary Bonding:* The assembly and laminating of thin sheets of material into flat or curved structures with the aid of pressure and warm- or hot-setting resin adhesives.

*Secondary Bonding:* The assembly of solid components or sections already laminated with the aid of adhesives or other similar components. The attachment of fittings or assembly of reinforcing stringers or ribs to plywood skins constitutes secondary bonding operations.

Metal adhesives, wood adhesives, acid-resisting adhesives, textile adhesives, linoleum cements, rubber cements, and paper adhesives are a few of the many end use classifications which prevail for adhesives. While useful to the layman they tell very little about the nature of the material which would help the engineer or chemist to predict their probable behavior. However, when used in conjunction with other methods of classi-

fication, they may help to clarify the method and the soundness of the application.

Typical end uses of the adhesives are discussed much more fully later in this book. However, it is possible to draw a few basic comparisons at this time: *Metal Adhesives*—Usually a rubber or chlorinated rubber base. Volatiles are preferable evaporated before the bonding is complete.

*Wood Adhesives*—Many glues of animal and vegetable origin are suitable, as well as the synthetics. Volatiles may diffuse through the relatively porous wood structure. When used for exterior purposes, there must be care in selecting adhesives with durability to weather extremes.

*Acid-Resisting Adhesives*—Chemical processing and storage tanks or conduit find various inorganic and synthetic resin types to be quite satisfactory.

*Paper Adhesives*—Starch, dextrans, proteins, etc. are employed extensively in the field of paper adhesives. This field includes many thousands of applications to envelopes, stamps, book-binding, labels, corrugated papers, etc.

*Textile Adhesives*.—Starches and dextrans both as adhesives and sizing agents are used in the textile field. Rubber base adhesives may be employed for specialty laminating operations, while synthetic resins are being used more extensively for sizing purposes. Adhesives or sizing agents used on automatic machinery must set quite rapidly. They usually should not interfere with the flexibility of final product.

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## Chapter 2

### Phenolic Resin Adhesives

Long prominent among synthetic resins has been phenol-formaldehyde, which has enjoyed extensive applications in molding, laminating, casting, surface coating, and adhesive fields. While the formation of phenolic resins was the subject of many early efforts<sup>1, 2, 3, 4</sup>, the commercial developments of phenolic plastics date from Dr. L. H. Baekeland's patents and announcements, commencing in 1909<sup>5, 6, 7, 8, 9</sup>. However, phenolic resins as adhesives did not attain full scale commercial significance until introduced into the plywood industry in the United States in film form, in 1934 and 1935. Production abroad preceded work in this country by a few years<sup>10, 11, 12</sup>. It has been estimated that in 1934 there were in the United States less than a dozen multi-platen hot presses for plywood manufacture, which are the types best suited for handling phenolic resin adhesive<sup>13</sup>. Other multi-platen presses were in use by the laminating industry. With multi-openings the capacity of a hot press runs into many thousands of square feet per day, while for the slower setting room-temperature adhesives, the production output per press is very limited (see Figure 3).

While the commercial adaptation of phenolic resin adhesives was slow in getting started, the potentialities of phenolic resins in plywood manufacture have long been recognized. One of the first attempts to use them in this manner was recorded in a British patent<sup>14</sup>. In 1910 a French patent suggested the use of a phenolic resin film<sup>15</sup>, while Baekeland and Thurlow recognized the possibilities of phenolic resin adhesives in plywood manufacture in this country<sup>16</sup>. They also emphasized in their early work the possibilities of developing a hard, glossy surface which would withstand wear and mechanical abuse. Wood veneer treated with phenolic resin could also be bonded to metal and ceramic surfaces, it was indicated. McLain also contributed to the early adaptation of phenolic resins to the bonding of wood veneers<sup>72</sup>. He applied the resin from a solution, and after evaporation of solvent, pressed the surfaces together under heat and pressure.

Today phenolic resin adhesives have attained a much more impressive industrial acceptance, due in large measure to manufacturing refinements which have made available adhesives suited to different combinations of

pressure, temperature and time of cure. The phenolic-resin adhesive manufacturer has also actively cooperated in mechanical developments of pressing facilities, as well as in chemical developments. The adhesives industry also is indebted to phenolic resin manufacturers for focusing attention upon the importance of water-resisting, boil-proof glue lines for permanence of plywood quality. Before the advent of synthetic-resin adhesives, the absence of adequate water and fungi resistance in glue lines restricted many applications involving outdoor exposure or locations of high humidity. The numerous aircraft applications of synthetic resin-bonded plywood testify to the wide acceptance of these adhesives.

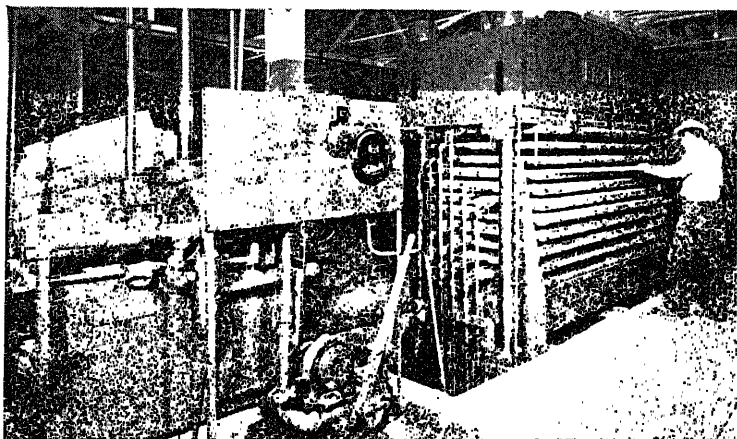
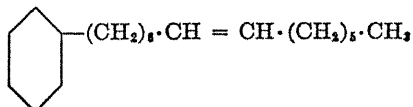


Figure 3. Multi-opening hot press for plywood manufacture

In order to understand the various characteristics which may be developed into phenolic resin adhesives it is necessary to examine the various types of phenol-aldehyde resins and the methods of preparing them. Prior to the first World War all the phenol used in the United States was obtained largely as a by-product of the coke industry, though shortly thereafter the supply was derived from the coal-tar industry. Synthetic phenol prepared from benzol, however, now is the chief source.

Aside from pure phenol, other phenolic constituents have been considered in adhesive manufacture, including mixed cresols (ortho, meta, and para); resorcinol; 3,5-dimethyl phenol (now being synthesized); and "Cardanol" ( $C_6H_4OH \cdot C_{14}H_{27}$ )\*. Of these, resorcinol base adhesives are of most

\* Phenolic constituent derived from cashew nut shell liquid to which is ascribed the following structure<sup>18</sup>.



recent commercial adaptation<sup>17</sup>. The resorcinol employed in adhesive manufacture is about 95 per cent pure, the balance consisting of small amounts of phenol, catechol, and other constituents. It is, however, about 60 cents per pound, making it higher in cost than other phenolic constituents for resin manufacture.

Among the aldehydes which are reacted with phenolic constituents to form resin adhesives are formaldehyde, paraformaldehyde, acetaldehyde and furfuraldehyde, in their respective order of importance. In the resin formation, formaldehyde may be preferred, though for the purposes of activating the resin prior to use dry, powdered paraformaldehyde is widely used.

The rate of reactivity of the phenols with aldehydes depends upon the identity of the phenolic as well as of the aldehydic constituent. The phenolic portion is quite influential, however, and the rate of resinification

Table 6  
(Data by Sprung)

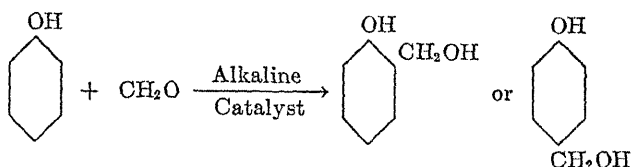
Phenol	Rate Constant
3, 5 xlenol	0.063
<i>m</i> -cresol	.0233
phenol	.00811
<i>p</i> -cresol	.00287
<i>o</i> -cresol	.00211

with formaldehyde, as may be empirically observed, shows resorcinol, 3,5-xlenol, and phenol in decreasing order. The addition reaction products of phenols and its homologs with paraformaldehyde have been studied by Sprung, and typical results are shown in Table 6<sup>19</sup>, though one of the most comprehensive studies of phenolic homologs and formaldehyde has been reported by Granger<sup>20</sup>.

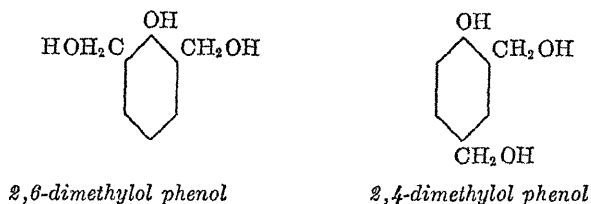
In early investigations on phenol-formaldehyde resins, Baekeland proposed stages A, B, and C to distinguish between low molecular weight, initial condensates; fusible, but difficultly soluble stage B; and infusible, insoluble stage C. These expressions are still freely used, though the distinction between the various stages is not very clear. The mechanism of phenol-formaldehyde condensation-polymerization, first suggested by Raschig<sup>21</sup> and later agreed upon by other investigators, represents cross-linking, forming a rigid spatial network of main valences through methylene linkages<sup>22, 23</sup>. It depends upon the existence of three reactive positions upon the phenolic nucleus, two ortho and one para to the hydroxyl group. The occupation of these positions with, for example, various

alkyl groups, decreases the ability of the phenol to form a thermosetting polymer, accounting for the low rate of resinification of ortho and para cresol. Where slow-curing laminated structures are required, this control feature is desirable, though for the more rapidly curing adhesive formulations, fast curing phenol-aldehyde resins are generally preferred. Of course, storage life and stability of the adhesive must be considered, and it is a usual practice to withhold some of the methylene-forming groups until the adhesive is ready for use.

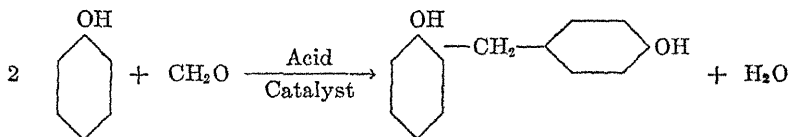
The nature of the catalyst as well as the molar proportions determine the course of the reaction from the start<sup>24</sup>. In the presence of alkaline catalysts, ortho and para hydroxybenzyl alcohols are formed from the reaction of phenol and formaldehyde:



It may likewise be assumed that in the presence of a molar excess of formaldehyde (most adhesives are prepared with a molar excess of 1.1 to 2 of formaldehyde to 1 of phenol), dialcohols may also be formed<sup>25</sup>:



On the other hand, resinification under acid conditions leads to the formation of diphenyl methane:



It has been suggested that the partially polymerized phenolic resin is best represented by a linear polymer possessing fewer than six phenolic nuclei, with methylol groups in the reactive positions in the presence of an excess of formaldehyde<sup>26</sup>. The infusible and insoluble state is attained upon further condensation-polymerization and formation of a large complex cross-linked molecule. The character of the net-work formation is difficult to evaluate due to the insolubility of the material, though various

theories have been proposed to explain its structure. Such studies are of fundamental importance to an understanding of the adhesive forces developed. It is quite likely that the presence of unreacted methylol groups, unreacted reagents, and portions of the polymer with a low degree of polymerization entrapped in the larger net-work formation will influence the adhesive properties, as well as the finished structure. The existence of unreacted agents in the capillaries and pores of the sponge-like skeleton of large macromolecules has been suggested in the isogel theory of Houwink<sup>27</sup>, though in more recent investigations a preference is shown for the spherocolloidal theory<sup>28</sup>. Small clumps, called spherocolloids, are formed in a highly polymerized resin, surrounded by a continuous phase of lower molecular weight components. In a more recent experiment, Carswell examined net-work formation of phenoplasts in advanced states of cure by the swelling of phenolic films in acetone. The technique was applied to a study of the effect of catalyst concentration, reactant ratios, and temperature of cure. It was observed that increasing molar ratios of formaldehyde contribute to more bridges in the final cure state. A structure was proposed for phenoplasts involving spherocolloidal particles (measuring  $1 \times 10^{-3}$  to  $3 \times 10^{-4}$  sq. mm. area) interlinked by substantial methylene bridges<sup>29</sup>.

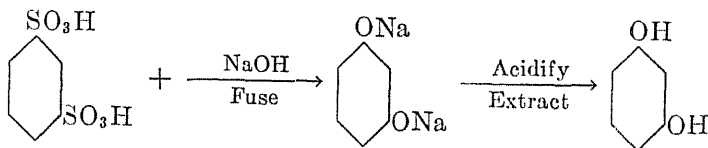
While studies have been directed toward the reaction of phenol with aldehydes, very little basic work has been reported on the effect of side groupings or substituted phenols on the adhesive properties of the final products. Some work has indicated the suitability of meta-substituted phenols for adhesive manufacture; 3,5-dimethylethyl phenol and 3-methyl-5-isopropyl phenol are reacted in the presence of sodium hydroxide to form a phenolic resin condensate compatible with various alkyds, useful as an adhesive and coating material<sup>30</sup>. In another example the reaction product of a substituted phenol and formaldehyde are cooked in the presence of a mild NaOH solution and tung oil to form an oil-soluble adhesive product<sup>31</sup>. Both of these examples indicated coating as well as adhesive applications. Coatings as well as adhesives entail problems of adhesion to miscellaneous surfaces.

### Resorcinol-Formaldehyde

The reaction of resorcinol with equimolar proportions of formaldehyde takes place with considerable vigor, and at a rate that is normally difficult to control. The development of various controlling features has, however, made possible a low-temperature setting adhesive which has wide adaptability to the bonding of various woods, rubber, and organic plastic products. Before its commercial introduction in 1943 pioneer work was done by Pennsylvania Coal Products Company in cooperation with A. J. Norton,

A number of basic patents on the resorcinol-formaldehyde reaction were taken out by Novotny in 1930, 1931 and 1932. These are reviewed later.

Resorcinol,  $C_6H_4(OH)_2$ , may be prepared by the fusion of *m*-benzenedisulfonic acid with alkali:



It has long been recognized as an active resin-forming ingredient and a number of early resorcinol-aldehyde resins were prepared<sup>32, 33, 34</sup>; most of these investigators reported rapid transformations to infusible, insoluble substances. The increased reactivity of resorcinol over phenol is explained in part by the existence of an additional reactive position between the two

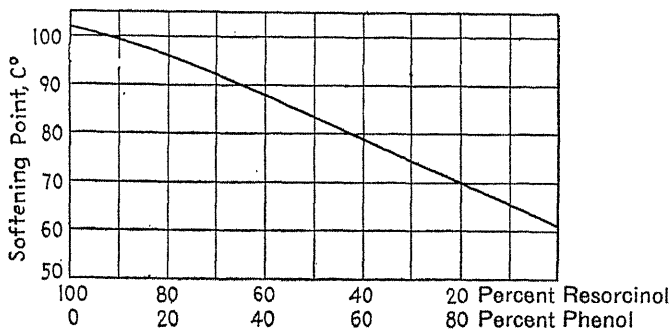


Figure 4. Resins formed by reacting 1 molecule of resorcinol-phenol to .67  $\text{CH}_2\text{O}$ . (Rhodes).

hydroxyl groups and at the other positions of the benzene ring. The increased reactivity is also evident in the fact that cure time, cure temperature, and catalyst concentration are all less for resorcinol than for a typical phenol or cresol-formaldehyde reaction. In fact, the substitution of part of the phenol by resorcinol in a typical reaction with aldehydes will in general effect an improvement in the rate of attaining the infusible, insoluble stage C resin<sup>35</sup>. For example, approximately 0.13 mole of resorcinol, 0.50 mole of phenol, and 1 mole of paraformaldehyde are heated at  $100^\circ$  to give a product of rapid reactivity.

Other practical uses of resorcinol in assisting the hardening of phenol-formaldehyde resins are evident in the addition of 5 to 10 per cent to casting compositions which have a large molar excess of formaldehyde. Curing times are reduced to as little as  $1/4$  of the original. Somewhat similar improvements have also been noted with 3,5-dimethyl phenol. The addition of resorcinol-formaldehyde to a phenol-formaldehyde resin results

in an increase in the softening point, when for example, the reaction proceeds with an excess of phenolic constituents. For example, in Figure 4 Rhodes showed a relationship between the softening point and relative proportions of phenol and resorcinol<sup>36</sup>. These fusible resins are in turn reacted with further methylene groups to attain an infusible, insoluble state. Resorcinol-resin adhesives may have their cost reduced by including phenol in the reaction.

From the point of view of the adhesive manufacturer, the increased reactivity of resorcinol has its advantages as well as disadvantages. The advantages are quite apparent when full cure is realized in as short a time as possible after application of the adhesive. For example, in Figure 5 the shear strength of birch plywood prepared with resorcinol-formaldehyde

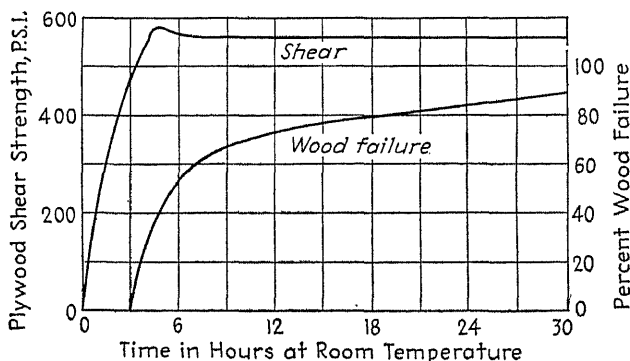


Figure 5. Birch plywood strip shear strength shown as function of cure time at room temperature—resorcinol—formaldehyde adhesive.

adhesive is shown as a function of curing time at room temperature<sup>17</sup>. The attainment of 100 per cent wood failure is viewed as the optimum in a wood adhesive. It is also very significant that the pH of this resorcinol-resin adhesive is 7.2, practically neutral, and hence it is less likely to be detrimental to the cellulose. The shear strengths of the plywood are obtained according to testing procedures outlined in government specifications for aircraft plywood<sup>37</sup>.

The commercial forms of resorcinol-formaldehyde adhesives are furnished in a solvent, which decreases viscosity as well as inhibits resinification; the amount of volatiles is approximately 40 per cent. The resorcinol type of adhesive is activated by the addition of catalysts, usually paraformaldehyde, which provide the methylene groups necessary to complete resinification. After activation the life at room temperatures of 75 to 80°F is generally limited to 2.5 to 3 hours, as determined by the rate of viscosity rise of the adhesive after activation. Much above 4000 centipoises it is a

rather heavy paste, difficult to apply by brushing or by a glue spreader roll. In Figures 6 and 7 are the results of tests performed in the writer's laboratory, the viscosity of a typical resorcinol-formaldehyde adhesive ("Penacolite", G-1131) is recorded as a function of time at room temperature after incorporation of catalyst. The adhesive properties were further evaluated after different times in the glue pot, and after different open assembly periods, noted as 0 open assembly time, 10 minutes open assembly time, and 20 minutes open assembly time. Open assembly time refers to

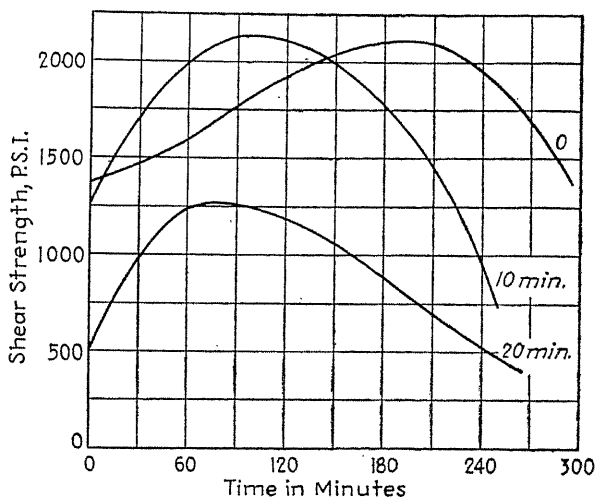


Figure 6. Characteristics of resorcinol formaldehyde adhesive on sanded phenolic laminates. Variables shown are time in minutes after adding catalyst, before adhesive is applied and three open assembly periods after application of the adhesive. All assemblies were cured one week at room temperature before test.

the time lapse after applying the glue as a film to the surfaces being bonded and assembling parts; during this interval the volatiles are given a chance to evaporate. Most room temperature-setting adhesives have open assembly times of less than 30 minutes. The tests illustrated in Figures 6 and 7 were performed upon sanded laminated phenolic, canvas-base plastics, and all failures occurred in the glue line; there were no phenolic laminate failures. Apparently a peak in effectiveness is reached after one to two hours pot time. Approximately 15 minutes were taken to incorporate the catalyst in the adhesive liquid, with constant stirring.

The separation of paraformaldehyde, which is part of the resin-forming reagent, from the main liquid is indicative of the storage problem which would be encountered if a full molar combination was effected before the material was ready to be applied. In a number of patents on the manufacture of resorcinol-formaldehyde resins, Novotny places emphasis upon

the necessity of reacting less than 1 mole of formaldehyde with 1 mole of resorcinol. In one early patent when equi-molar proportions were employed, Dry Ice was introduced into the resorcinol-formaldehyde resin to chill the reaction, as well as to make possible the production of a hollow, porous body<sup>38</sup>. However, in other patents, resorcinol is reacted with less than 1/2 molar paraformaldehyde, and additional paraformaldehyde is added to harden the resin<sup>39</sup>; also resorcinol is reacted with less than molar formaldehyde, with additional reagents capable of forming methylene groups added in a subsequent step to harden the resin<sup>40</sup>. In more recent work leading to the development of "Penacolite" resorcinol-formaldehyde

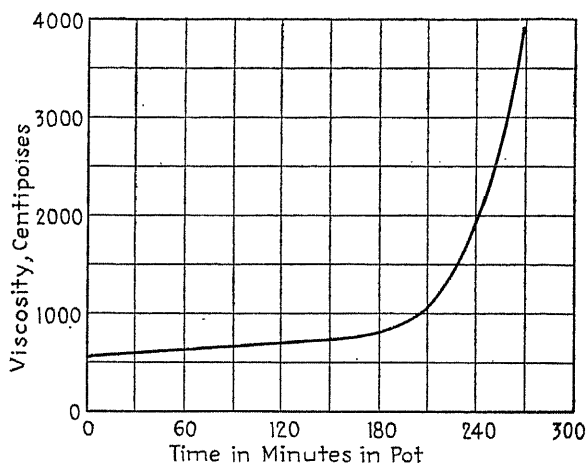


Figure 7. Viscosity stability of resorcinol— $\text{CH}_2\text{O}$  adhesive after activated with catalyst.

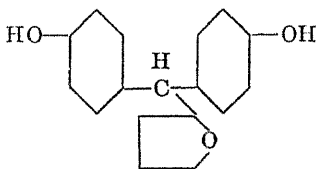
adhesives, Norton reacts a molar excess of resorcinol to formaldehyde under slightly acidic conditions in the presence of a liquid diluting medium. The aldehyde is added slowly so that there is no excess at any one time<sup>41</sup>. Heating is continued under reflux until the reaction goes to completion and the resin is dissolved in a volatile solvent. Rhodes uses only enough formaldehyde to form a fusible resin, withholding the catalyst until near the completion of the reaction<sup>42</sup>. There have also been some significant British patents bearing upon resorcinol-formaldehyde resins. One of these describes the improved adhesion of rubber surfaces by pre-treatment with an aqueous solution of resorcinol-formaldehyde<sup>43</sup>. Another describes the bonding of layers of material with condensation products of formaldehyde polymer and resorcinol or phenol<sup>44</sup>. A phenol-resorcinol glue for aircraft and marine construction has been described<sup>45</sup>. Low-temperature setting qualities and neutral glue lines are featured.

With respect to low temperature setting qualities, it should be noted however, that when the resorcinol adhesives set at temperatures below 70°F., inferior joint strength will result. The subsequent raising of temperature may not necessarily improve the results.

**Applications.** Resorcinol-formaldehyde resins are being used as bonding materials for various woods, plastics, and rubber products. Low-pressure polyester laminates, primary wood structures, methyl methacrylate sheets, and polyamide sheets are among the materials effectively bonded with this type of resin. Fabrication processes involving sheet plastics are not always effectively assembled with rivets, screws, and other mechanical devices. The availability of strong, durable adhesives will augment these fabrication methods. Numerous wood assemblies for aircraft and naval requirements have been successfully completed with resorcinol type adhesives. At the close of the second World War, the production of resorcinol resin adhesives averaged 300,000 to 400,000 pounds monthly<sup>45a</sup>.

#### Phenol-Furfural Resins and Furfural Additions to Phenol-Formaldehyde Resins

Furfuraldehyde, as a substitute for formaldehyde, gives rise to a number of useful resinous products with phenol. Furfuraldehyde, a brown liquid with a boiling point of 157–167°, has a viscosity of 1.35 centipoises at 38°. It is not readily compatible with water. In reaction with phenol, the only water to be removed after the resin has formed is due to the condensation polymerization involved, and in this respect differs from formaldehyde which requires the water present in the formalin (37 per cent formaldehyde) to be removed. Furfural reacts much like other aldehydes, though as pointed out in a subsequent chapter on miscellaneous thermosetting resins, much stronger catalysts than are ordinarily present in phenol-furfural condensations are necessary to effect a reaction through the furane ring. A portion of the phenol-furfural polymer may be visualized as follows:



Portion of the phenol-furfural polymer

In the manufacture of phenol formaldehyde bonded abrasive wheels furfural proved to be a useful plasticizer. Coating the surfaces of the abrasive material with a wetting agent such as furfural rendered the phenolic adhesive more fluid and permitted its more effective distribution. This principle was recognized early in the manufacture of abrasive grind-

ing wheels and filtering media<sup>46, 47</sup>. For example, approximately 1000 grams of silicon carbide granules, depending on grit size, are wetted with 20 cc. of furfural in one instance and with various other salts such as sodium fluoride in another. These increase the tendency of the adhesive to flow and spread into intimate contact with abrasive particles. The phenol-formaldehyde resin in powdered form is added to the approximate extent of 8 per cent by weight of the mixture. When the resin is thus added to the moistened grains, the furfural dissolves enough resin to coat the grains uniformly over their surface with the solution of furfural and resin, insuring a well bonded structure. In another process the phenol-formaldehyde resin is mixed directly with the abrasive grains and molded into useful structures by heat and pressure<sup>48</sup>, though the process is simplified and cheapened by the addition of a few per cent of furfural or high-boiling aldehydic body<sup>49</sup>. In this manner the abrasive particles are firmly cemented together. Further modifications have also been used involving the formation of a binder for abrasive grains by reacting together tung oil, phenol, and methylene hardening agents<sup>50</sup>.

Furfural has also been employed as a hardening agent and modifier for phenol-butyraldehyde condensation products produced with an acid catalyst. The end product shows adhesive properties<sup>51</sup>.

One of the first patents dealing with the preparation of phenol-furfural resins also suggested reaction with resorcinol<sup>52</sup>. Furfural in this example is also modified with furfuramide. An advantage is claimed in good release from metal mold surfaces.—A moldable composite body in which the individual layers of fibrous material are cemented together with a phenol-furfural condensation product or an animal or vegetable glue, is described by Novotny<sup>53</sup>. The face of this assembly however, was rich in phenol-furfural resin capable of taking a molding impression as in the manufacture of phonograph records. Whereas these earlier developments of phenol-furfural employed acid catalysts, in more recent patents basic catalysts such as potassium carbonate are employed. In a preferred example, 100 parts of phenol are reacted with 75 parts of furfural and 2 per cent of potassium carbonate at 250–300°F for two hours. This fusible, soluble resin may then be combined with further hardening agents such as hexamethylenetetramine to attain an infusible, insoluble polymer<sup>54</sup>. Smaller amounts of catalyst are employed in a similar manner to produce heat-reactive, liquid phenol-furfural resins<sup>55</sup>. These latter resins would be of greater interest to adhesive manufacture inasmuch as the percentage of solvents required is relatively smaller than when the resin is a solid.

Synthetic resins produced from phenol, formaldehyde, and furfural have been known for some time. The general effect of the furfural is to impart increased fluidity and penetrating quality to the varnish. As an example,

50 pounds of phenol-formaldehyde resin are dissolved in 100 pounds of alcohol and 20 pounds of furfural<sup>56</sup>. The improvement in flowing qualities has also been noted in molding compounds<sup>57</sup>. Cresols or xylenols are simultaneously reacted with furfural and formaldehyde to produce varnishes useful in impregnating and bonding paper and cloth<sup>58</sup>. Much of the early work on phenol-furfural resins was performed and reported by Beckman and Dehn<sup>59</sup>. Besides the use of furfural as a plasticizer, Delmonte has recently reported the combination of furane resin polymers copolymerized with phenol-formaldehyde resins<sup>60</sup>.

A heat-reactive resin prepared from 50 parts of phenol and 50 parts of furfural in the presence of sodium carbonate is ground and mixed with powdered rubber. The dry mixture is applied to a metal surface, a layer of rubber is added and the whole is vulcanized under pressure<sup>61</sup>. Acid or alkali condensations of resorcinol and furfural are reported to yield tanning substances better than the best vegetable tanning agents for leather. The leather so treated does not shrink in boiling water<sup>62</sup>.

### Adhesives from Phenol-Formaldehyde Resins

The most important members of the phenol-aldehydic series of resins from the standpoint of volume produced and the greatest number of applications are the phenol-formaldehyde resins. Produced in the form of emulsions, powders, liquids, and films, they have fulfilled many adhesive problems. In some instances the function of bonding two surfaces together was all that was required, while in other examples, the phenolic resin adhesives have fulfilled the dual role of adhesive and impregnant. As an impregnant the physical properties of the material being bonded may be improved in some respects by the treating resin.

Early use of phenol-formaldehyde as a general-purpose adhesive or glue was recognized by Redman, who condensed one mole of hexamethylenetetramine with phenol in the presence of a solvent. Heat and pressure were employed to convert this adhesive to an infusible state<sup>63</sup>. A cement for sealing the joints of metal pipes was prepared by dissolving 100 parts of phenol-formaldehyde resin in 100 parts of alcohol, containing 20 to 50 parts of monochloronaphthalene, glycerol, or castor oil. Seven to eleven parts of hexamethylenetetramine were added as catalyst<sup>64</sup>. Another early phenolic resin for cementing glass and metals was formed by reacting benzoic acid, glycerol, phenol, and formaldehyde<sup>65</sup>.

As may be expected, early developments of phenol-formaldehyde resin adhesives were combined with prevailing glues at that time to form useful adhesive products. For example, a phenol-formaldehyde condensate was combined with partially hydrolyzed glue protein, with an optional addition of casein or blood albumin<sup>66</sup>. A protective film of albumin was used

to keep the proteins dissolved<sup>67</sup>. In another instance, a cementing composition for abrasives to steel discs was prepared from a mixture of shellac and phenol-formaldehyde. Chalk, pumice, and ferric oxide were employed as fillers<sup>68</sup>.

As early as 1928, phenol-formaldehyde condensation products were modified with cellulose ethers, such as ethylcellulose, to control the hardening of the compounds, as in the preparation of experimental laminated structures<sup>69</sup>. Modifications of phenol or cresol-formaldehyde resins with cellulose esters, cellulose acetate and cellulose nitrate, as well as plasticizers, also contributed to the preparation of adhesives for safety glass manufacture<sup>70</sup>. In the preparation of safety glass, a strong resilient bond must be obtained between the organic, transparent plastic interlayer and the sheets of plate glass. Numerous useful adhesive preparations for these articles are described in subsequent chapters.

While various patent references draw attention to the potentialities of phenol-formaldehyde resin adhesives, it was not until the appearance of phenolic resin film that the synthetic adhesives began to enjoy widespread commercial applications in the plywood field. While thin films of blood albumin have been employed to unite wood veneers together<sup>71</sup>, thermosetting synthetic resins require tissue paper as a carrier, because of their more brittle character. This was first observed by McLain, who impregnated thin cloths or papers with phenol-formaldehyde resins, and employed these for bonding wood veneers<sup>72</sup>. He employed paper, fabric, or felted material and used heat and pressure to consolidate the assembly. Glycerol may be added to reduce the brittleness of phenolic resin films<sup>73</sup>. In the preparation of commercial phenolic resin films, the resin is prepared with a basic catalyst and before the point of water separation it is deposited upon thin paper and dried<sup>74</sup>. The thickness is about 2 mils, with approximately 2 parts of resin to 1 of paper in one of the commercial phenolic resin-treated papers. Cresols may also be used in partial replacement of the phenol<sup>75</sup>. While complete details are given in the chapter on the bonding of wood, it may be noted that the phenolic resin film ("Tego" film) is cured at temperatures of 280–320°F, with uniform moisture content in the wood veneer layers of 7 to 9 per cent. This phenolic resin film is suited to many types of flat, hot press operations, insuring a uniform distribution of adhesive at all the glue lines. Where curved and compound shapes are required, however, it is generally necessary to employ the adhesive in a liquid or varnish state, as the thin film is considered too brittle for such operations. Phenolic resin deposited upon two-way creped paper has been utilized for the adhesive layer in the preparation of compound curved shapes. The creped paper will permit much more stretching at the glue line during cure of the resin. Rowe creped webs with as little as 2 lbs. phenolic adhesive per 1000 sq. ft.<sup>75a</sup>

In other applications of phenolic resin films, it has been reported that metals have been joined to wood with phenolic resin films. In this example, 40–50 per cent phenolic resin, 4–6 per cent rosin, and 2–3 per cent castor oil are applied in solution form to an unsized paper 0.04 to 0.05 mm thick<sup>76</sup>. In applications other than film forms, phenolic resins have been blended with non-drying oil, after treatment with rosin, to be used as adhesives<sup>77</sup>. In more recent extensions of the film idea, phenolic resin adhesives have been applied to an absorbent material on one side of a wire gauze, permitting the preparation of composite laminates<sup>78, 79</sup>.

Dry phenolic resin film in plywood manufacture has enjoyed many successful applications. In the first technical paper on this subject published in this country, Sorensen described the results upon veneers bonded with imported film<sup>11</sup>. The effect of the variables of pressure, bonding temperature, moisture content of veneers, and time were examined. At the same time the imperviousness to mold and fungi growth were demonstrated in comparison with animal, albumin, and casein glues, which rapidly lost their effective shear strength within a few weeks. The influence of moisture content of veneers and curing temperature upon the shear strength of birch plywood bonded with dry phenolic glue film is pronounced, good cures being obtained at 320°F and 8 to 10 per cent moisture<sup>80</sup>. Complete pressing schedules are reported by Perry and Bretl<sup>12</sup>. Among earlier uses suggested for plywood manufactured with this adhesive were: radio cabinets, phonographs, fine furniture, desks, bookcases, outdoor furniture, luggage, patterns, doors, exterior plywood, service trays, etc.

During World War II, much of the aircraft plywood manufactured in this country employed phenolic resin-bonded plywood because of its superior weathering and mold resistance. It possessed outstanding water resistance at the glue line, and it was possible to form and shape such plywood, after appropriate steaming, into simple curved sections such as seats for aircraft purposes, serving trays, airplane wing tips for training ships, etc. In addition to the bonding of plywood, an important use developed for phenolic resin film in the manufacture of Masonite diestock, which is pressed at 2500 psi and at a temperature of about 350°F. Layers of wood fibers with lignin activated by explosion processes<sup>81</sup>, are bonded into tough, durable sheet stocks up to several inches in thickness. Layers are approximately 1/8 inch thick and between them are phenolic resin films.

In addition to the use of single layers of phenolic resin film in manufacturing plywood, Bernhard, Perry, and Stern report on the use of multiple layers of phenolic resin film at bonding pressures up to 2500 psi<sup>82</sup>. Observations indicated that some penetration of the phenolic resin into the wood structure occurred, and the amount of synthetic resin employed

influenced the strength of the plywood. The strength of the highly compressed plywood appears to increase in direct proportion to the density, though the increase in shear strength takes place more rapidly.

In Table 7, certain data are reproduced from the paper of Bernhard, Stern, and Perry, for 1/8, 1/16, and 1/48-inch birch veneers, all alternate cross-layered, with specific pressures of 500 psi.

In interpreting the results shown in Table 7 it is important to recognize that the improvement in strength is not due only to the synthetic resin, but that compressed wood alone is stronger than natural wood. The relationships between woods of different densities and their physical characteristics have already been extensively investigated<sup>83</sup>. Further data on this subject are presented in the chapter on wood adhesives.

The application of phenolic resin-impregnated high-strength Mitscherlich papers to aircraft plywood, both as a bonding agent and as protective

Table 7. Influence of Phenolic Resin Film on Physical Properties of Birch Plywood<sup>82</sup>.

Construction		Specific Gravity	Compression Strength (psi)	Tensile Strength (psi)	Shear Strength (psi)
No. and Thickness of Wood Veneers	No. of Phenolic Film Layers				
Solid Birch	—	0.63	6200	10,100	2020
9 1/8 in.	8	0.77	7890	11,840	6060
17 1/16 in.	16	0.72	7980	13,920	6330
69 1/48 in.	68	1.05	11,720	19,160	11,540
73 1/48 in.	72 × 2	1.105	13,300	19,800	14,520
63 1/48 in.	62 × 3	1.05	12,590	16,930	12,280

coatings, was investigated by Delmonte<sup>84</sup>. While good resistance to moisture permeation was evident for impregnated papers as surface protective coatings, the plywood strip shear test values decreased with increased papers in the glue line. However, there was evidence of increased tensile properties of the wood, due to pre-stressing of wood in compression because of differences in the coefficients of thermal contraction as the paper-plywood assembly was cooled. More recently, several organizations have manufactured good exterior waterproof plywood, following these same principles<sup>85</sup>.

Aside from the phenolic resin films, other forms of this adhesive have attracted attention in recent years. Dispersions of phenol-formaldehyde resins in hot water have been aided with sulfonated oils, and proteins as stabilizers<sup>86</sup>. Water-dispersed phenolic resin adhesives were also described by Sontag and Norton<sup>87</sup>, and Dent proposed colloiddally dispersed phenolic resins for plywood manufacture<sup>88</sup>. In another case, a phenol-aldehyde

resin varnish intended for plywood manufacture is dispersed in water with an acid pH. Substantial quantities of blood albumen are added after reneutralization<sup>89</sup>. Aqueous dispersions of phenol or resorcinol-formaldehyde resins are employed to improve the adhesion of rubber to different materials<sup>90, 91</sup>.

### Water-Soluble Phenol-Formaldehyde Resins as Adhesives and Impregnants

Due in large measure to the pioneer efforts of the Forest Products Laboratory at Madison, Wisconsin, much attention has been focused upon the phenolic resin impregnation of woods and other cellulosic materials<sup>92</sup>. While early efforts to stabilize wood with natural resins and waxes have been reported, the particular advantages of water-soluble phenol-formaldehyde resins were emphasized<sup>93</sup>. Highest anti-shrink efficiencies (determined by the retardation in dimension changes of the control for the average of three 4-week relative humidity cycles between 30 and 90 per cent) were obtained with water-soluble phenol-formaldehyde resins. In preliminary examinations of white pine, oven-dried blocks were immersed in different synthetic-resin forming solutions, of relatively low molecular weight. These included phenol, formaldehyde, linseed oil, and furfural combinations. The highest anti-shrink efficiency and the highest resin pickups were obtained with an aqueous solution of 1 mole of phenol, 2.5 moles of formaldehyde, and 0.6 mole of concentrated ammonium hydroxide. The wood was placed in the resin-forming solution for at least a day, and after adequate diffusion had occurred was oven-cured at 105°. Various commercial resins, including phenolics, alkyds, and polystyrene, were examined upon several woods, and it was observed that a decrease of anti-shrink efficiency was obtained with resins of increasing degree of prepolymerization or decreasing polarity. Gluing tests revealed that the synthetic resin-treated wood could be satisfactorily glued with animal or casein glues, as well as hot-press phenolic resin glue films.

These early studies were extended to include the resin treatment of wood veneers and the development of improved types of plywood<sup>94, 95</sup>. One of the purposes of this study was to minimize checking on plywood surfaces; for while it was observed that phenol-formaldehyde and urea-formaldehyde resin glues developed plywood with superior weathering properties, the severe stresses caused by weather extremes will set up differential stresses in plywood to ultimately produce face checking. In bonding the resin-impregnated veneers with protein, animal, vegetable, and synthetic-resin adhesives, it was observed that longer assembly periods were necessary because resin treatment of the wood reduced its tendency to absorb glue solvents. Moisture vapor transmission of veneers impregnated with

phenol-formaldehyde resins was greatly decreased in comparison with untreated woods, and fire resistance was improved. Recognition of the improvements in plywood resulting from the impregnation of wood veneers with synthetic resins was consistent with the now generally recognized superiority of synthetic-resin glues for outdoor exposure. Brouse, reporting on the results of 4-year tests on plywood, indicated the superiority of the phenol-formaldehyde adhesive for plywood<sup>96, 97</sup>.

The extent to which wood swells in resin-forming ingredients was pointed out by Stamm and Seborg as indicative of the affinity of the wood for these materials; aqueous phenol-formaldehyde resin solutions caused more swelling than water alone or other resin-forming constituents. Preference is indicated for a slightly polymerized phenol-formaldehyde resin solution with a pH of 8. The resin diffuses to the cell wall and is believed to be chemically combined to free OH groups in the cellulose. Optimum resin contents are in the neighborhood of 27 to 30 per cent. Lower laminating pressures were indicated for resin-impregnated wood, though greater difficulty was encountered in gluing to the more highly polished compressed face of the wood<sup>98</sup>.

The plasticizing action of resin-forming ingredients upon wood at polymerization temperatures was the subject of another report<sup>99</sup>. Resin-treated compressed wood ("Compreg") has been employed for making complete airplane propeller blades. Whereas it was believed necessary to employ additional adhesives at the glue line to laminate resin-impregnated wood veneers into plywood, it was indicated in a later report that good glue joints can be obtained without additional adhesives beyond those resins employed for impregnation, if higher moisture content was present (7.5 per cent at the time of pressing)<sup>99</sup>. Ten different commercial water-soluble resins were evaluated for their usefulness in wood impregnation, and were found to develop equal anti-shrink efficiencies.

More critical examinations of the physical properties of laminated, phenolic resin-impregnated compressed wood revealed that the impact strength of water-soluble phenolic resin-impregnated woods had fallen off to 1/7th of that of untreated, uncompressed wood<sup>100</sup>. An improvement of impact strength to 1/2 that of untreated wood was made possible by increasing laminating pressure to bring the density from 1.1 to 1.3; by drying at 130°F; by keeping the resin content under 30 per cent; and by more closely controlling temperature at the center of the laminate.

In the meantime, while the employment of alcohol-soluble phenol-formaldehyde resins as impregnants and adhesives was found not to give as good moisture resistance as the water-soluble types, there were nevertheless a number of organizations employing alcohol-soluble phenolic resins because of the higher impact strength of the laminated products. One

manufacturer reported values as high as 40,000 psi tensile strength, and a modulus of elasticity of  $4 \times 10^6$  psi for phenolic resin-impregnated woods, though lower values were reported for alcohol-soluble phenolics elsewhere<sup>101</sup>. Higher phenolic resin contents were experienced because of penetration into the lumen as well as the cell wall structure of the wood tracheids. Some of the data reported were as follows<sup>102</sup>:

Table 8. Influence of Resin Content and Laminating Pressure on Water Absorption (Alcohol-soluble Phenolic Resin).

Laminating Pressure (lbs. per sq. in.)	Resin Content (%)	Specific Gravity	Water Absorption (% in 24 hours)
1200	40	1.27	5.8
500	40	1.15	8.5
1200	55	1.36	1.5
500	55	1.17	5.1

Laminates prepared with the above type of phenolic resin-impregnated veneers were machined into airplane propellers. In laying up such veneers prior to laminating, varying lengths were selected, so that a variable density construction was obtained with the low-density portion nearest the tip of the blade and the high-density portion nearest the hub. Not all laminated wood aircraft propellers employed resin impregnation. Some relied upon phenolic resin film alone, such as the English Jablo propeller, and brass strips over the leading edge<sup>103</sup>.

In a comparison between alcohol-soluble phenol-formaldehyde resins (estimated molecular weight 500–100) and water-soluble phenol-formaldehyde resins (estimated molecular weight 150–200), Casselman distinguished between the effects of the two types of resin upon birch wood veneers as follows<sup>104</sup>:

Table 9

Property	Water-soluble Phenol-Formaldehyde	Alcohol-soluble Phenol-Formaldehyde
Specific gravity	1.35–1.37	1.34
Modulus of rupture (psi)	37,000–40,000	40,000
Modulus of elasticity (psi)	$3.0\text{--}3.6 \times 10^6$	$3.5 \times 10^6$
Impact (Izod-notched) (ft.lbs/in)	1.4–4.1	6–7
Compressive strength (psi)	25,000	25,000
Shear strength, parallel to grain (psi)	6–7000	6–7000
Water absorption (% in 24 hours)	1–2	4–6

In still another technique, referred to as the “spreader method” of impregnation, the resin is applied to the veneers as a surface coating on the conventional glue spreader, dried to a low moisture content, and then

is forced into the wood during the compression operation<sup>105</sup>. The manufacture of good "Compreg" is claimed, with higher impact strength than the resin diffusion method, though greater water absorption was observed. The plasticization of the phenol-formaldehyde resin by water has also been recognized as a convenient method of obtaining good penetration and bonding of plywood<sup>106, 107</sup>. Nevin prefers an aqueous cresylic acid formaldehyde solution of 900 to 2000 centipoises, containing 45 to 50 per cent solids.

Somewhat improved strength-weight properties may be obtained by chemical treatment of wood veneers prior to resin impregnation. Luce prepared a number of plywood laminates after delignifying the wood veneers by chemical digestion and replacing the lignin with synthetic resins. A very soft, pliable veneer is obtainable by a mild digestion of wood veneers, insufficient to break them down into fibers<sup>108</sup>. Likewise some mercerization of the wood veneers with sodium hydroxide solution and subsequent washing has been found by the writer to yield superior plywood laminates<sup>109</sup> when these veneers are bonded together.

In turning attention to the phenolic-resin impregnation of comparatively thick cross-sections of wood, it has generally been found feasible to adopt some special procedures for obtaining efficient penetration. For example, by applying the resin solution at the end of a green, sap-filled log, good penetration can be obtained as the resin displaces the sap<sup>110</sup>. One German practice removes the sap from the log by cutting away the bark and cambium, and withdrawing the sap at this location as pressure is applied to the solution at the end. After the resin-filled log has been prepared, it may be cut and kiln-dried to obtain a hard, superior type of wood product.

The impregnation of sections or veneers of wood 1/8-inch and thicker, with phenolic resins can best be accomplished by a vacuum-pressure technique. After applying a vacuum of about 27 inches for a few hours, the vacuum is broken by drawing water-soluble phenolic resin into the impregnating tank and covering the wood. This is followed by applying an air pressure of 20 to 60 psi for about 20 hours. After this tank impregnation the resin should be allowed to diffuse a few more days before baking, which should be done slowly to avoid checking the wood. The impregnation of these veneers can usually be aided by steaming the veneers before they are immersed in the resin solution.

Many types of resins have been proposed for the impregnation of wood veneers. Stamm and Seborg have mentioned urea-formaldehyde, alkyds, and polystyrene, though phenolics have proven to be more adaptable to commercial requirements. The higher molecular weight of the fully polymerized thermoplastics renders true penetration difficult. Even the thermosetting resins in an advanced stage of cure do not penetrate too effectively. A British patent citing water soluble resins of phenol, urea,

thiourea, and resorcinol-formaldehyde, indicates somewhat parallel trends in wood impregnation in that country<sup>111</sup>.

Plywood stabilization is also possible without resin impregnation through special heat treatment processes. Stamm describes a process of passing wood veneers continuously through a fused bath of a sodium or potassium acetate salt at 550°F.<sup>112</sup> A more practical technique was worked out however in the manufacture of "Staypak". Wood veneers with approximately 12 per cent moisture content are pressed at 300–360°F. under a pressure of 2000 psi. By this treatment the wood veneers are densified to an extent that springback tendencies are minimized. Wood veneers receiving this treatment are more stable than veneers not treated, and will contribute to a more stable laminated construction.

In summarizing the advantages and disadvantages of phenol-formaldehyde resin impregnation of wood veneers and lumber, it is important to recognize how closely it is associated with fundamental bonding problems. Impregnation may be viewed as contributing to bonding in three dimensions, while surface bonding at the glue line is a two-dimensional problem. Strictly speaking, for porous materials such as wood and cellulosic products, there is no true two-dimensional bonding, as some penetration is usually encountered. In conclusion, the methods of impregnating wood with synthetic phenol-formaldehyde resins may be described either as:

- (1) Diffusion of low molecular weight constituents into the cell walls, preferably in an aqueous medium, or,
- (2) Mechanical penetration into the pores of wood structure, usually through heat and pressure.

The chief advantages of resin treatment of wood are:

- (1) Stabilization of the wood structure, described as anti-shrink efficiency.
- (2) Improvements in physical properties run parallel to the increase in density, except for shear strength, which improves at a more rapid rate.
- (3) The presence of resin in the wood restricts moisture vapor permeation.
- (4) The uncured resin plasticizes the wood, permitting lower laminating pressures, at the time of bonding into plywood.
- (5) Chemical resistance of the wood to acids, mild alkalis, and solvents are improved considerably by phenol-formaldehyde resin impregnation.
- (6) Resistance of wood to mold and fungi growths is markedly improved.
- (7) Some improvement in fire resistance is obtained,

The chief disadvantages are:

- (1) The impact strength of the wood is lowered. For thermosetting resins, it appears that the better the penetration into the wood fiber structure, the more pronounced the loss of impact strength.
- (2) Cost of the plywood is raised.

(3) Subsequent gluing to impregnated wood is more difficult than with untreated wood.

Little has been said about the cost so far, but it should be noted that an economical way of applying resin impregnation is not necessarily to the entire plywood structure, but only to the face plies<sup>114</sup>. Resin treated veneers are used as face plies and untreated veneers as core stock. In preparing curved plywood shapes with wood veneers impregnated with phenolic resins, it is not always necessary to maintain a balanced construction, which is important to flat-press plywood<sup>115</sup>. The veneers are laid up in a direction favorable to the maximum stress. Less expensive cresylic acid-formaldehyde condensation products prepared under alkaline condensation have also been employed for bonding wood plies together<sup>116</sup>. For impregnating wood, sometimes a combination of alcohol and water may best serve for carrying the resin. Booth, with the aid of vacuum, applied phenolic resins in this manner<sup>117</sup>.

In other specifications the wood is soaked in water to remove soluble salts, dried, and then placed in an aqueous solution of a thermosetting resin<sup>118</sup>. The amount of water extractable is, however, relatively small. Niederhauser and Miller prepared a water-soluble resinous composition stable in cold aqueous solutions over a broad range of pH. Formaldehyde was reacted upon phenol in the presence of an alkaline catalyst and with a molar excess of 1.1 to 1.5 moles. This resin was then reacted with an inorganic sulfite (1 mole) to 3 to 8 moles of methylol phenol to form sulfonate groups<sup>119</sup>.

Water-soluble phenolic resins have been applied to other cellulosic materials both as adhesives and impregnants. In one interesting group of experiments at the writer's laboratories, thick kraft papers from 0.004 to 0.019 inch thick were impregnated with aqueous solutions of phenolic resins to a resin content of 40 per cent. The bonded laminates showed tensile strengths of 18,000 psi and a modulus of elasticity in flexure of  $2.0 \times 10^6$  psi, though water absorption was 9.0 per cent<sup>120</sup>. Particular advantages have also been observed for fiber-resin cores and relatively stiff face plies.<sup>121</sup> In this paper very interesting relationships are drawn between specific gravity and tensile or flexural strength for a 50 per cent phenolic resin and 50 per cent fibrous material bonded with the resin. They report more uniform resin distribution by forming the fibrous cores in a resin solution, rather than by subsequent impregnation of a fiber pad.

For a review of the contributions of phenolic resin-bonded plywood and resin-treated plywood to the nation's war effort, particularly in aircraft and naval fields, there have been many noteworthy papers calling attention to gliders, pontoons, training planes, pilots' seats, water tanks, droppable gasoline tanks, spars, monocoque constructions, and many others<sup>122, 123,</sup>

### Low-temperature Curing of Phenolic Resin Adhesives

While much of the flat press work in the production of phenolic resin-bonded plywood and many of the structural parts employing bag molding techniques and steam pressures utilize hot-setting phenolics, there are growing demands for low-temperature setting thermosetting synthetic-resin adhesives for general use. One important group of resin adhesives fulfilling this requirement is the resorcinol-formaldehyde type, though urea-formaldehyde and furane resin adhesives will also be discussed in other chapters. There are warm-temperature (around 60°) setting phenol-formaldehyde resins as well as types which will set at room temperatures of 25 to 30°C. The need for low-temperature setting adhesives for certain aircraft assemblies has been indicated a number of times<sup>130, 131</sup>. Low-temperature setting phenolic, melamine, and resorcinol-formaldehyde adhesives employed in the manufacture of ship stems, keels, and frames have shown a high percentage of wood failure even after twelve months' exposure to weather and salt water. As brought out previously the cure should preferably take place at temperatures above 70–80°F., because if below this range full strength will not be developed.

Alcohol or alcohol-water solutions of phenol-formaldehyde resins activated with various catalysts have served as low-temperature setting adhesives. The curing rate of most low-temperature adhesives is greatly increased by higher temperatures. Unlike the resorcinol-formaldehyde type of adhesive with a favorable pH for the glue line at about 7.0, the pure phenol-formaldehyde resins require much stronger catalysts to set at room temperature; strongly acid types are generally employed, with a pH in the neighborhood of 1.2 to 1.5 in some cases. This pH is quite severe upon the wood bond, leading to embrittlement of the wood fibers in the immediate vicinity of the glue line. The effect, however, is much less pronounced when the phenolic low-temperature cement is applied to the bonding of such articles as cast or laminated phenolics.

Very strong alkaline catalysts may be used to set up the phenolic resins at low temperatures, though these too can be as detrimental as strong acid catalysts. However, they have the further disadvantage of preparing a glue line which may be more susceptible to the effects of water, lacking the resistance of the acid-catalyzed phenolic specimens. As far as the art is known at the time of writing, the low-temperature activation of phenol-formaldehyde resin adhesives requires rather strong (OH<sup>-</sup>) or (H<sup>+</sup>) concentrations, a condition that can be modified only by partial replacement of the phenol with a more reactive constituent, such as meta-cresol, 3/5-dimethyl phenol, or resorcinol, or by the introduction of a large excess of methylene-forming reagents. The latter contingency, however, contributes to greater instability in the glue line. The storage life of the unac-

tivated low-temperature setting phenolic-resin adhesive is very short—in a number of cases not over 2 months at 70°F—though life is prolonged to about 6 months by storage at 50°F. After activation with a catalyst, the pot life of glue varies from about 2 hours at 90°F. to 4 hours at 70°F. When the adhesive is spread as a thin film in application to the surfaces to be joined, the open assembly time varies from 15 to 20 minutes at 90°F to 30 to 45 minutes at 70°F for a number of low-temperature setting phenolics.

There are no fixed rules to govern the amount of adhesive required for a particular job, though most resin adhesive manufacturers recommend certain glue spreads, which define the weight of liquid adhesive for 1000 square feet of surface. A typical spread for plywood may be 35 pounds of adhesive per 1000 square feet, for a single glue line. This may all be applied on one surface or preferably divided between the two surfaces to be pressed together. More or less of the adhesive may be required, depending upon the relative porosity of the surface. Excess loss of adhesive due to high surface porosity, or to low viscosity of the glue, permitting rapid diffusion, results in a "starved" glue line. The addition of a finely divided cellulosic filler, such as wood flour or walnut shell flour, screening at finer than 100 mesh, may be used with the adhesive for cellulosic surfaces. The filler may generally be added up to 15 per cent by weight of the adhesive. One specification calls for 1 to 20 per cent of 180-mesh wood flour in the adhesive<sup>132</sup>. In other instances diatomaceous earth may be used as a filler to increase the viscosity of the adhesive, though various combinations may be preferred. For non-porous materials, filler additions may be detrimental. As a matter of fact, the addition of fillers to thermosetting synthetic resin adhesives should be viewed with a good deal of caution because the filler may disturb the balance of low and high molecular weight components in a given resin solution, due to its preferential absorption of the low molecular weight portions. As will be discussed in a subsequent chapter on the theory of adhesion, the specific chemical adhesion of a resin for a given surface may be due to a proper balance of low and high molecular weight proportions within the resin.

### Miscellaneous Developments in Phenolic Resin Adhesives

There have been a large number of noteworthy developments and applications of phenol-formaldehyde resin adhesives which have been modified with other resins and adhesive substances. Because they indicate some of the background which has led up to the more widely used commercial types, they will be briefly reviewed and evaluated. In the early days of the manufacture of laminated safety glass, a number of synthetic resins were proposed for bonding the cellulose ester interlayer to the glass sur-

faces. Among these were dihydroxybenzophenones condensed with aldehydes, the condensation products being modified by glycerin or employed in conjunction with cellulose acetate<sup>133</sup>. Zinc chloride and aluminum chloride catalysts were specified in a subsequent development of this adhesive<sup>134</sup>. Urea-formaldehyde-phenol products were also employed experimentally as an adhesive in the manufacture of safety glass<sup>135</sup>. The adhesive was prepared by refluxing at 125° for 2 hours 150 parts of 40 per cent formaldehyde, 100 parts of phenol, and 20 parts of urea. Various plasticizers modified the adhesive formulation. Cellulose acetate was also blended in a mutual solvent with the urea-phenol-formaldehyde resin to make the adhesive<sup>136</sup>. Equal parts of xylene solution of Canadian balsam and alcohol solution of glycerol-phenol-formaldehyde resin are suggested as safety glass adhesive<sup>137</sup>.

A useful wood adhesive is described by Arnot, who prevents the precipitation of animal glues on the addition of cresol-formaldehyde condensates, by partially hydrolyzing the glue and adding a protective colloid of blood albumin. The cresol-formaldehyde condensation product was added to the animal glue partially hydrolyzed by heating with water and sodium bicarbonate in an autoclave at 130° for two hours<sup>138</sup>. In other examples, Jeschke heated glue and glycerol together, and followed this by the addition of a phenolic resin to prepare an adhesive for linoleum<sup>139</sup>. A leather substitute was prepared by binding together leather scrap with a phenolic resin modified with albumen or keratinous substances<sup>140</sup>. By heating phenolic resin with alkaline catalyst to form a varnish, followed by a weak acid and dispersing agent, and subsequently reneutralizing, it has been possible to introduce a substantial quantity of blood albumen with the resin<sup>89</sup>. Phenolic constituents may also serve to plasticize animal glue formulations, such as the addition of cardanol (cashew nut shell liquid), in a wide range of proportions to gelatin<sup>141</sup>. Good punching qualities have been found for phenol-cardanol-formaldehyde laminates<sup>142</sup>, though cresol-formaldehyde resins have fulfilled most of the requirements for punching grades.

Aqueous dispersions of phenol-formaldehyde resins as adhesives have been prepared with the aid of emulsifying agents such as saponified sulfonated oils or triethanolamine. Glue and casein have been introduced as stabilizers in such dispersions<sup>143</sup>. Advantages have been found through an intimate mixture of alkali soluble phenol-formaldehyde resin powder with sodium metasilicate, when used as an adhesive<sup>144</sup>.

As additives to various materials, phenolic resins have helped the adhesive properties. For example, concentrated distillery slop with the addition of alkali and phenolic resins falls in this category<sup>145</sup>. Aliphatic olefins in combination with phenolic resin adhesives are reported<sup>146</sup>. Rosin modifications of phenolic resins followed by the addition of non-drying oils have been proposed as an adhesive<sup>147</sup>.

Even inorganic materials such as Portland cement have been combined with phenol-formaldehyde resins to form adhesives recommended for linoleum<sup>148</sup>. Phenol-lignin resins, activated with hexamethylenetetramine, have been found useful in bonding plywoods in some Russian developments<sup>149</sup>.

Modification of the phenol-formaldehyde resin with other synthetic resins has long been practiced in obtaining adhesive formulations. Water-soluble methyl vinyl ketones are reacted with aqueous solutions of phenols and aldehydes to obtain a water-soluble adhesive product<sup>150</sup>. Powdered magnetic substances insulated with a layer of polyacrylic resins are bonded with heat-hardenable resins such as phenol-formaldehyde<sup>151</sup>. Phenol reacted with polyvinyl acetate and paraformaldehyde forms a resinous product which, dissolved in organic solvents, makes a useful adhesive, which has been applied to safety glass<sup>152</sup>. Another form of urea-phenol-formaldehyde resin with good adhesive properties is prepared by reacting 1 mole of phenol with 1.5 moles of formaldehyde at 50–70° in sodium hydroxide solution. After vacuum removal of water, further reaction is continued with dimethylolurea<sup>153</sup>. Esters of anacardic acid (derived by esterifying cashew nut shell liquid), are reacted with phenol-formaldehyde resins at 285° to obtain materials with good adhesive properties<sup>154</sup>.

Rayner and de Bruyne report good adhesive bonds between woods and organic plastics through combinations of aniline-formaldehyde and phenol-formaldehyde. The aniline-formaldehyde is prepared by reacting 1 mole of aniline, with 0.8 to 1.0 mole of hydrochloric acid and 1.2 to 1.5 moles of formaldehyde, followed by precipitation with alkali. This is added to an aqueous solution of phenol-formaldehyde resin<sup>155, 156</sup>. Heat-curing at 140° and 200 psi is recommended for this combination.

Resorcinol in an aqueous solution containing free formaldehyde is combined with a urea-formaldehyde resin and ammonium chloride in another adhesive product<sup>157</sup>, while a cold set adhesive for plywood veneers is formed from urea-cresol and formaldehyde, containing a soluble borate and glycerol. This latter adhesive is hardened with phosphoric acid<sup>158</sup>. Another phenol-urea-formaldehyde adhesive is recommended for the cementing of glass applicator rods or droppers to phenolic bottle caps. The resin is prepared by reacting 7.5 pounds of urea with 7.5 pounds of phenol in 3 gallons of 37 per cent formalin at 6.0 to 6.5 pH at 70° for 3 hours. For good water resistance the proportion of phenol should be at least 50 per cent. Prior to baking, the adhesive contains 80 per cent solids, and tartaric acid is employed as an accelerator<sup>159</sup>. Soybean meal impregnated with a cured phenolic resin and urea-formaldehyde as resin binder has served as a cement<sup>160</sup>. Norton prepared a fusible phenol-aniline-formaldehyde-castor oil resin modified with glyceryl phthalate as an oxidation re-

sistant binder for brake linings and clutch facings<sup>161</sup>. A cold process for preparing an aqueous solution of blood in a cresylic acid resin was described by Golick and Dike<sup>162</sup>. A smooth suspension at a pH of 7.75 to 9.0 was formed. Phenol-formaldehyde plus glycol chlorohydrin and *p*-toluene sulfochloride is described as an adhesive<sup>163</sup>.

Phenol-formaldehyde resins plus polymerized acrylic or vinyl esters and boric anhydride are recommended as adhesives<sup>164</sup>. Abrasive particles are also bonded with phenolic resins, modified with alkyds for increased flexibility<sup>165</sup>. Chlorinated diphenyls as plasticizers for phenolic resin adhesives are reported to improve flexibility<sup>166</sup>, while ethylene glycol is mixed with water-soluble phenolic resins for the same purpose, as a cement for thermosetting moldings<sup>167</sup>. Ethylene glycol or glycerol with methyl or ethyl orthosilicate as modifiers for a phenol-aldehyde condensation product are described by Spirk as adhesives for articles made from various plastics<sup>168</sup>.

The inclusion of metal with phenolic-resin adhesives may occur as a foraminous metal surface and tissue paper, absorbent of the liquid phenolic resin, for making plywood<sup>169</sup>, or as a finely divided powder, as in a basing cement for incandescent lamps, where aluminum powder has been specified<sup>170</sup>. Commercial varieties of lamp basing cements do not however, employ metal powder, but rely on phenolic cements alone.

Some understanding of the recent developments in water-soluble phenolic resin adhesives may be obtained from an examination of recent patents. Dike dissolved powdered phenolic resin adhesive in 10 per cent sodium hydroxide and employed the solution in the bonding of wood veneers<sup>171</sup>, while Niederhauser and Miller condensed phenol or meta cresol with formaldehyde in presence of alkaline catalyst and then reacted an inorganic sulfite in the proportion of 1 mole of sulfite to 3 to 8 moles of phenol alcohols<sup>119</sup>. Van Epps produced a boil-resistant phenolic resin adhesive by reacting phenol with a large molar excess of formaldehyde in a strong sodium hydroxide solution<sup>172</sup>.

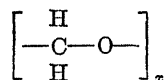
Cone has developed some valuable combinations of phenolic resins with proteins to form weather resistant bonds in plywood manufacture<sup>173</sup>. The protein to phenolic resin ratio is rather broad 1.8/8.5 to 8.5/1.8. The phenolic resin is produced under alkaline conditions, followed by the addition of a blood solution.

Increased interest is also being shown in synthetic rubber-resin adhesives. One combination of butadiene-acrylo nitrile with phenolics has served as a binder for a heavy duty frictional element<sup>179</sup>. In another example, a depolymerized rubber and phenolic resin are dissolved in a mutual solvent to form a useful adhesive<sup>180</sup>. As an aid towards dispersing rubber in a phenol solution, oxygen is passed through until the rubber is dissolved. Formaldehyde is added and reaction continued until the resin is formed<sup>181</sup>.

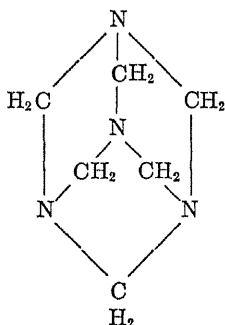
A stable adhesive has also been prepared by dissolving a fusible phenol-furfural resin in a solvent, condensing in the presence of an acid and then adding a solution of natural or synthetic rubber <sup>182</sup>.

### Catalysts or Hardening Agents for Phenol-Formaldehyde Resins

Important to the final cure of most phenol-aldehyde synthetic resin adhesives are various catalysts or hardening agents, as they are sometimes called. These catalysts are described as methylene-forming reagents in some instances, or acids and alkalis in other examples. While straight formaldehyde has been employed in expediting the cure of some resorcinol type adhesives, paraformaldehyde is now generally preferred. On heating paraformaldehyde, formaldehyde is liberated. The structure generally ascribed to paraformaldehyde is as follows, usually forming a mixture of several polymers: It is a white powder, soluble in water.



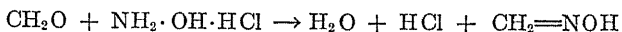
Another useful hardening agent frequently employed in connection with phenolic-resin adhesives is hexamethylenetetramine, which will liberate ammonia and free methylene groups. It has the further advantage that in reacting with the phenol-formaldehyde resin no water is formed, as in the case of paraformaldehyde. The value of employing dry hexamethylenetetramine as a hardening agent was recognized early by Aylsworth<sup>173</sup>. The structure of hexamethylenetetramine is generally considered to be as follows:



Among the acid catalysts, a number of various types have been employed, ranging from concentrated, strongly ionized types to those produced by chemical decomposition. At least in one example, the catalyst is identified as 3 parts of concentrated hydrochloric acid plus one part of water. Twenty parts of this accelerator are employed to 100 parts of

resin<sup>174</sup> to form a cold-setting resin adhesive. Hydrochloric acid as catalyst has been definitely specified in certain wood-bonding operations<sup>175</sup>.

When traces of free formaldehyde are present in the phenol-formaldehyde resin, an aqueous solution of hydroxylamine hydrochloride will serve as an effect catalyst because of the liberation of hydrochloric acid. This does not take place instantaneously but requires at least several minutes, depending on initial pH and temperature.



*Hydroxylamine-  
hydrochloride*

When strong acid catalysis may be required, various acids with high ionization constants may be employed, including phosphorous acid, phosphoric acid, trichloroacetic acid, maleic acid, oxalic acid, and others. Generally acids such as lactic and acetic are too weak to promote low-temperature setting of the adhesive, though they may be employed for a high-temperature cure. Among other catalysts used for high-temperature curing are ethyl and methyl sulfate, which will decompose into their respective alcohols and sulfuric acid, and hence establish conditions favorable to the resinification of the phenolic.

The inclusion of strong acid catalysts in viscous resins invites certain problems of attaining adequate dispersion, generally necessitating some wetting agent or detergent. One manufacturer even found it expedient to employ a color indicator in with the phenolic adhesive to indicate distribution of the acid catalyst<sup>176</sup>.

Among the alkaline catalysts, various materials have been employed, including ammonium hydroxide and sodium hydroxide. Barium hydroxide and calcium hydroxide are also effective in promoting resinification of polyhydric phenolic resins. Ethylenediamine and diethylenetriamine are also mentioned as catalysts for phenolic resin adhesives<sup>177</sup>. Other organic bases with relatively high ionization constants such as triethanolamine, and diethylamine and trimethylamine are also employed.

In a later chapter on the theories of adhesion, an effort will be made to correlate the data on phenolic resin adhesives and their catalysts with their behavior toward various materials being bonded.

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## Chapter 3

### Urea and Melamine Resin Adhesives

Urea-formaldehyde resins have been prominent for many years as thermosetting synthetic-resins adhesives, in addition to the recognition they have attained as light-colored molded or laminated plastic materials. While urea-formaldehyde resins do not possess the moisture resistance of the phenol-aldehydes they nevertheless have advantages in their good water solubility and light colors before reaching the infusible, insoluble state. Powdered urea resin derivatives may be readily dissolved in cold water and applied as impregnants or adhesives. Various formulations are distinguished by their room temperature-setting characteristics. At the start of 1946 urea and melamine adhesives exceeded molding compositions of the same resins by almost three to one. Their price range lay under 20 cents per pound, making them quite economically attractive.

As in the case of phenol-formaldehyde resins, the history of urea resins begins with the miscellaneous laboratory efforts and early recorded patents of numerous individuals. Goldschmidt, in early investigations of the reaction of urea and formaldehyde in neutral and acid media, produced certain white granular condensation products<sup>1</sup>, while in later reactions under alkaline conditions he produced mono and dimethylolurea<sup>2</sup>. In the first United States patent on urea-formaldehyde resins in this country, John pointed out their advantage as adhesives. In preparing a resin from 5 parts of 40 per cent formalin with 1 part of urea in the absence of catalysts, he stated<sup>3</sup>:

"If the ingredients are caused to react only during a short period, the product of condensation is still soluble in water. This solution is highly adhesive and, when dried, leaves the condensation product in the shape of a perfectly colorless product which is transparent like glass and insoluble in all inert solvents.

"In this stage, therefore, a glue is produced which sticks in a cold state to all objects, of preference with smooth surfaces, such as glass, metals, etc. The substance may also, besides other applications, be used for filling root canals in dental surgery, or as a lacquer which can be directly laid on without addition of spiritous or such like solvents."

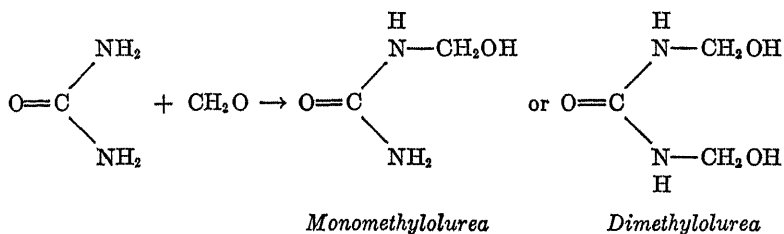
Even in an early British patent, F. Pollak recognized the usefulness of

urea- and thiourea-formaldehyde resin adhesives, and the salts of strong acids as accelerators. Among these were identified ammonium chloride, ammonium nitrate, and ammonium sulfate<sup>4</sup>. The same hardening agents were again identified in a later patent on urea-formaldehyde resins<sup>5</sup>.

Much of the background on the development of urea-aldehyde resins has been discussed at length by Ellis, who reviews the historical aspects, as well as the more recent practice in the developments of moldings and coatings from these resins<sup>6</sup>. As in the case of most commercial plastic materials, the wide scale application of urea resins was preceded by the development of ample supplies of low-cost raw materials. This was marked in 1935 by the production of synthetic urea in this country, from by-product gases, ammonia and carbon dioxide. Emphasis was placed on urea-formaldehyde resins rather than thiourea-formaldehyde resins, because of improved performance during molding, though from an adhesive point of view, the latter materials possess many desirable qualities.

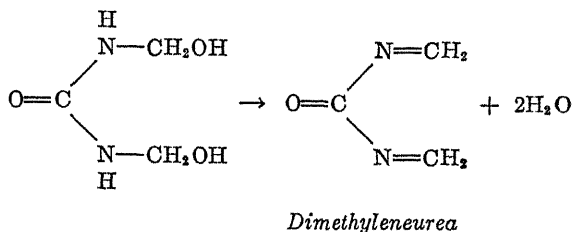
Considerable research on the mechanism of the urea-formaldehyde resinification was done by G. Walter and associates<sup>7</sup>. This study has been of particular value in revealing the nature of the urea-resin polymer formed through condensation of methylol ureas, and the existence of chemical groupings which may contribute to the adhesive properties. It is generally recognized that the principal influences on the reaction of urea with formaldehyde are the molar proportions of the constituents, the hydrogen ion concentration, the temperature, and the time of reaction. In fact the pH is closely controlled in commercial practice, even to the extent of carefully buffering the residual acidity of formaldehyde due to traces of formic acid.

In the reaction of urea with formaldehyde, the nature of the reaction products depends, as in the case of phenolics, upon the H-ion concentration; when it is carried out under alkaline conditions, monomethylolurea or dimethylolurea may be formed, depending on the molar proportions of formaldehyde to urea.

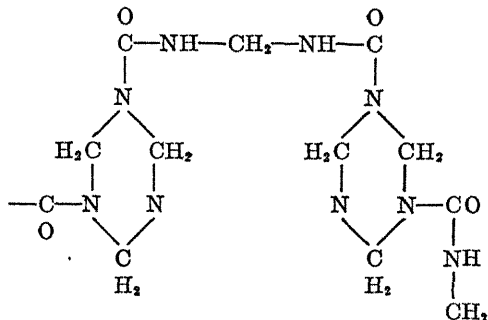


From the standpoint of functionality, the possibility of forming a thermosetting resin may be anticipated from the dimethylene urea, formed on loss of water from dimethylolurea. The tetra-functional dimethylene

urea would give a thermosetting structure. The formation of dimethyleneurea is favored under acid catalysts, though dimethyleneurea does not exist as such, polymerizing from this state to a higher molecular weight.



While further polymerization of dimethyleneurea has been surmised to form a cross-laticed, thermosetting molecule, recent investigations by Marvel and co-workers<sup>181</sup> demonstrate a structure based upon the reaction of urea as an amino-acid amide. In such a molecule, the amine ( $\text{NH}_2$ ) would react with formaldehyde to yield methylene-imine derivatives which would trimerize, while the amide ( $\text{CONH}_2$ ) would react with formaldehyde to yield methylene bis-amide links between the rings. The structure of the urea-formaldehyde polymer proposed by Marvel is as follows:



Results indicate that the final cured resin contains free methylol groups in a series of urea residues interlinked by methylene bridges. It is not necessary to have 2 moles of formaldehyde per urea molecule to form the thermosetting polymer, inasmuch as monomethyleneurea is capable of forming a two-dimensional polymer cross-linked at various intervals by a dimethylene urea. Unlike phenolic resins, urea-formaldehyde resins remain substantially soluble in water during resinification. Their hydrophilic qualities may be explained in part by the presence of the free methylol groups. At the time of setting or gelling, however, transformation takes place rapidly as the cross-linking of molecules takes place, with the formation of the infusible and insoluble structure. In studies of adhesion it is important to identify the presence of these free unreacted groups, which may show particular affinity for certain surfaces due to their polar

characteristics. The free methylol groups appear to possess an unusually good affinity toward cellulosic structures.

Less than two moles of formaldehyde per mole of urea has been shown to yield a more stable resin, which does not gas (due to liberation of formaldehyde) during molding and which has minimum water absorption<sup>8</sup>. A urea-to-formaldehyde ratio of 1:1.5 to 1.8 is generally preferred in preparation of the resin. The stronger the acidity, the more rapidly will the infusible, insoluble polymers be formed. The urea-resin adhesives are particularly interesting because of the ease with which they may be cured at room temperatures with mild acids and acid-forming salts. The problem of forming a stable liquid urea resin adhesive material is quite difficult, inasmuch as they tend to gel at room temperature within a few months, much like the partially polymerized liquid phenolic types. At present, preference is shown for a dry urea resin powder and filler, which is activated on the addition of water. In commercial practice, the urea resin is formed at a relatively low temperature and dried without hardening of the charge. In one commercial process the reaction is carried out at a pH of 5 to 6; by keeping the temperature at 20 to 30°, the formation of irreversible gels, which tend to occur under acid conditions (such as "Goldschmidts" compound  $C_5H_{10}O_3N_4$ ), is prevented at the lower temperatures. Drying takes place below 60° to produce the heat-reactive powder<sup>9</sup>. On the other hand, other commercial processes show preference for carrying out the reaction under alkaline conditions (pH 7.5 to 8.0) to form an aqueous resin syrup<sup>10</sup>.

The developments of urea-formaldehyde resins have emphasized the urea-formaldehyde condensation reaction rather than the thio-urea-formaldehyde reaction. Aside from observing the superior water resistance of the thio-urea compounds<sup>11</sup>, a careful comparison of the relative merits of the two materials has not been reported. One factor which has militated against the use of thio-urea-formaldehyde has been the tendency of the sulfur to attack steel during molding operations. This factor, however, is of less consequence in adhesive problems, and the presence of thio-urea in the condensation product should help the water resistance of urea-resin adhesives as well as contribute to the good adhesive properties. Pollak has pointed out the possibility of reaction at the sulfur atom in forming dimethylol thiourea<sup>12</sup>.

Adhesive products have been prepared from combinations of urea and thiourea reacted upon paraformaldehyde in the presence of water<sup>13</sup>. The polymer was mixed with water to form a useful adhesive paste. On the other hand, a cold-setting adhesive was prepared from condensation products of urea, thiourea, and formaldehyde with acid-forming salts<sup>14</sup>. In further modifications of their urea-thiourea-formaldehyde adhesives,

Taylor and Keller recommend concentrating the resin while still in a hydrophilic stage<sup>15</sup>, by removing excess water.

### Modifications of Urea-Formaldehyde Resins

Numerous efforts have been recorded on the modification of urea resin adhesives with other high polymers, either because of the stabilizing effect of the other polymers, acceleration of cure, or toughening action on final film. For example, Benteli proposes the combination of a urea-aldehyde condensation product with nitrocellulose and a plasticizer<sup>16</sup>, while water-soluble resin adhesive solutions from combinations of urea-aldehydes and phenol-formaldehydes have been suggested<sup>17</sup>. Urea-formaldehyde resin adhesives in an organic solvent were blended with various synthetic resins and cellulose esters for use as adhesives as early as 1925<sup>18</sup>.

Modification with starch may be presumed to be a likely consequence, considering the mutual compatibility with water. In order to improve the uniform dispersion of the adhesive on wood surface and obtain the desired degree of viscosity, starch may be added<sup>19</sup>. This development outlined the preparation of a urea-formaldehyde resin glue for wood veneers, whereby an acid-reacting compound inert to formaldehyde is added to the solution just prior to hot-pressing. Other urea-formaldehyde condensation products added to partially hydrolyzed starch by Glarum and Thomas are also significant<sup>20</sup>. The addition of 15 per cent urea-formaldehyde resin to a starch adhesive (based on dry weight) greatly improved water resistance without altering manufacturing conditions for corrugated paper-board<sup>21</sup>. This combination enabled the manufacturers of corrugated shipping containers to meet the stringent requirements of over-seas shipments. Ammonium chloride was introduced to set the urea resin.

Bowen and Dike collaborated in the preparation of urea-formaldehyde resin adhesives modified with zinc chloride, alone and in combination with starch, protein, gum arabic, or animal glue<sup>22, 23</sup>. Here is a typical example of the preparation of their condensation product: to 1100 parts of commercial formalin is added 200 parts of zinc chloride. After the zinc chloride is dissolved, 400 parts of urea are added and the mixture is heated to 75°, held there for 40 minutes, and cooled. A liquid resin is claimed which has a life of many months. To make a coating adhesive, 20 parts of this liquid solution are added to a solution of 3 parts of animal glue and 2 parts of thin boiling starch in 25 parts of water. Insolubilizing of the coating may take place on the addition of acid-forming reagents. Dike points out that the zinc chloride in this adhesive functions like sulfur in rubber treatment. At 105° the adhesive sets in one-third the time of the phenolic. A bond stronger than wood is obtained<sup>24</sup>. In a further patent, dry powders of zinc chloride-urea-formaldehyde are prepared by reacting 2 to 57 parts of

zinc chloride with 100 parts of urea and 250 to 300 parts of formalin, and spray-drying at 80° to produce a powder. This powder can be spread as a glue solution, 0.3 pound of water to each pound of glue<sup>25</sup>. In another development self supporting non-reinforced films of zinc chloride-urea-formaldehyde, were prepared with aid of triethylene glycol and  $H_3PO_4$ <sup>26</sup>.

Blood albumen has been employed as a modifying agent for urea-formaldehyde resin adhesives. Salts of strong acids are used as hardening agents for these combinations<sup>27</sup>. Hot-setting urea-formaldehyde resins, combined with phenol-formaldehyde products, are described as good adhesives for wood<sup>28</sup>. Especially effective for rapid hardening is resorcinol. The wood veneers in this case are bonded at 100°.

The condensation of methylolurea in an acidified monohydric alcohol with the addition of cyclic alcohols yields resins useful as adhesives or lacquers, and resins which may be combined with cellulose esters or ethers. In one example, urea and methylcyclohexanol are reacted with paraformaldehyde in ethanol to form an adhesive product<sup>29</sup>. Urea-formaldehyde resins have also been condensed in the presence of water-soluble cellulose ethers, such as methylcellulose, to form adhesives. It is also interesting to note that this same reference directs attention to dialdehydes such as glyoxal in lieu of formaldehyde<sup>30</sup>. Glyoxal is now being produced in commercial quantities. Besides methylcellulose, other water-soluble synthetic resins have been blended with urea or thiourea formaldehyde, including polyvinyl alcohol and polyvinyl ethers. The combination was effected in the presence of water soluble hydroxides of trivalent metals such as  $Al(OH)_3$ <sup>31</sup>.

Other high polymers not soluble in water have nevertheless been blended with urea-formaldehyde when prepared in the form of an emulsion. For example, 2 to 30 per cent methyl acrylate, applied to a cellulosic sheet as an emulsion before impregnation with a urea-formaldehyde resin, is claimed to yield a sheet material suitable for laminating or bonding purposes<sup>32</sup>. Urea resin modified with a small proportion of alkyd resins have been employed in the manufacture of abrasive belts<sup>33</sup>.

The treatment of urea-formaldehyde condensation products with water-soluble aliphatic amines until the viscosity is substantially increased yields valuable adhesive products<sup>34</sup>. Comminuted cellulosic fillers such as wood flour or disintegrated pulps, when impregnated with benzyl alcohol before incorporation into the urea-formaldehyde adhesive, will reduce cracking tendencies in thick glue lines, which is quite pronounced for ureas<sup>35</sup>. Crazing tendencies are due to volumetric shrinkage during cure and the evaporation of volatiles.

By mixing an aqueous solution of urea-formaldehyde resin with powdered, hardened synthetic resins, an adhesive product particularly useful

for linoleum is prepared<sup>36</sup>. This same combination is practiced upon a wood adhesive. To 67 per cent urea-formaldehyde resin and 33 per cent water are added a fine-ground phenol-formaldehyde resin in the stage C form. This method suggests an outlet for cured phenolic scrap. An acid-type catalyst is required for final hardening of the urea resin<sup>37</sup>. Partially polymerized phenol-formaldehyde resin added to the aqueous solution of urea-formaldehyde has been shown to improve stability of the urea resin adhesive to boiling water<sup>38</sup>, though commercial practices in this country show a preference for thiourea. This adhesive was recommended for pasteboard, vulcanized fiber, textiles, and woods.

Just as phenolic-resin adhesives were made available in thin film form, so have the urea-formaldehyde resins been prepared in this manner. A urea-formaldehyde solution with a pH of 3 to 6 was impregnated into a thin tissue paper by Rayner<sup>39</sup>, while an alcohol solution of urea-formaldehyde was applied to thin paper for the bonding of wood veneers<sup>40</sup>.

Pretreatment of finely divided wood flour for urea resin adhesives appears to have some advantages. Brookes impregnated wood flour with its own weight of cresol and then mixed it with ten times its weight of urea-formaldehyde solution<sup>41</sup>. In an even broader practice of this art, wood flour is treated with either a urea, phenolic, or alkyd resin of blood albumen, prior to incorporation with an aqueous solution of urea resin adhesive<sup>42</sup>. Preference is, however, expressed for an impregnant in the wood meal which is capable of reacting with the urea resin condensation product. From 5 to 20 per cent is indicated. Among the impregnants specified are polyacrylic acid amides, stearic acid and diethylenetriamine, and urea-formaldehyde in beechwood flour<sup>43</sup>. Dearing and Meiser prefer wood flour less than 0.02 millimeter in diameter, which they claim is important to the spreading of the urea resin adhesive<sup>44</sup>.

Proteins such as casein have been specifically employed as modifiers for urea-formaldehyde resin adhesives. They are generally added to an alkaline aqueous medium<sup>45</sup>. Besides the use of blood albumen with urea resins already described<sup>27</sup>, there are other noteworthy examples. Menger developed an adhesive for cellulosic products, involving urea-formaldehyde and up to an equal quantity of blood albumen. While the initial reaction takes place in the presence of a small amount of trisodium phosphate, the final combination with albumen is effected in the presence of ammonium chloride<sup>46</sup>. Animal glues in cemented assemblies obtained improved water resistance by addition of urea-formaldehyde resins<sup>47</sup>.

Starch additions to urea-formaldehyde are frequently described in the patent literature. In the preparation of urea adhesives from urea and hexamethylenetetramine, Kraus employs starch as a filler<sup>48</sup>, and Rangel follows the same procedure<sup>49</sup>. In the latter application, the urea resin

and starch filler are applied to one surface and the hardening agent to the other. Starch, tripoli, and calcium sulfate are mentioned as fillers for urea- or thiourea-formaldehyde resin adhesives by Rayner<sup>50</sup>; in another process starch is reacted simultaneously with urea and formaldehyde<sup>51</sup>.

The dilution of urea-resin adhesives with relatively low-cost fillers has often been mentioned as one of the cardinal advantages of this type of material, because it permits the costs to be adjusted to the quality of the work being performed. In an analysis of the combination of extenders with urea-resin adhesives, one of the adhesive manufacturers prepared an interesting table, parts of which are reproduced herewith<sup>52</sup>:

The quality of the adhesive, its strength and its water resistance fall off markedly with an increase in filler content, and type "D" in the table above is suited only for furniture applications not requiring high strength, such as mirror backs or dust covers, etc.

Table 10.

Ingredients	Straight	"A"	"B"	"C"	"D"
Urea resin and catalyst (lbs)	108	108	108	108	108
Water (lbs)		60	100	150	200
Extender (flour)		70	100	150	200
Solids content (%)	65	60%	55%	54%	53%
Cost per liquid pound	\$0.12	\$.061	\$.0497	\$.0406	\$.0350

Within recent years attention has been focused upon the foam type of adhesive as an efficient means of applying the glue to a porous surface, such as in plywood manufacture. The application of aqueous resin solutions to very thin veneers has its disadvantages in causing swelling of the veneers and subsequent warping. The adhesive, applied as a foam or thin film, tends to correct this condition<sup>53, 54</sup>. Various foaming agents, such as butylated naphthalene sulfonic acid, are recommended, while the foam is formed by a fine distribution of generated gases such as carbon dioxide<sup>55</sup>. Small amounts of calcium sulfate were observed to stabilize the urea resin foams<sup>56</sup>.

### Catalysts for Urea-Formaldehyde Resin Adhesives

A large number of catalysts have been employed in the hardening of urea-resin adhesives. Their choice is determined in many instances by the manner in which the adhesive has been manufactured, that is to say, whether it is a dry powder, liquid, or foam. Generally, the H ion concentration of the catalyst is determined by the temperature at which the adhesive is intended to set. Many of the refinements in urea-resin adhesives

within recent years has been occasioned by the development of delayed-action catalysts which permit relatively long working life and open assembly time for the adhesive, followed by rapid setting after assembly, to reduce the time under pressure.

F. Pollak<sup>4</sup> was among the first to recognize the usefulness of salts of strong acids, such as ammonium chloride, ammonium nitrate, and ammonium sulfate. The formation of the free acid in the presence of free formaldehyde, which reacts upon  $\text{NH}_3$ , is quite pronounced. Numerous room temperature-setting adhesives employ these catalysts, alone or in combination with acids<sup>14</sup>. The chief objection to immediate activation of the adhesive with catalyst is the short pot life and the need for rapid assembly time. One mechanical solution was the distribution of the hardening agent or catalyst on one surface to be glued, with the adhesive on the opposite surface<sup>57</sup>. Phosphoric acid, ammonium chloride, and aluminum chloride were mentioned as catalysts for this type of application<sup>58, 59</sup>.

Much interest has centered upon the use of urea-resin adhesives in the form of dry powders, which tend to be more stable than aqueous solutions. In one preparation, urea, thiourea, and catalysts were mechanically mixed with powdered paraformaldehyde<sup>60</sup>. The addition of moisture activated this mass to form the resin. A more interesting process is described by Kraus and Fisch, whereby a non-heat-hardenable urea-formaldehyde resin is prepared from urea, formaldehyde, and hexamethylenetetramine, so proportioned that there is a deficiency of methylene cross-linking agents. This forms a dry, stable preparation which may in turn be hardened by addition of an acidic hardening agent and a formaldehyde yielding compound such as paraformaldehyde<sup>61</sup>. Among the catalysts mentioned are sulfuric acid, oxalic acid, and ammonium salts of strong acids. Ammonium sulfate is particularly mentioned as a rapidly acting catalyst<sup>62</sup>.

In another technique, Menger coats the urea-resin adhesive with wax or asphalt, which melts below the hardening temperature. In this way he avoids premature hardening<sup>63</sup>. For hot-setting urea adhesives, various catalysts are proposed which act only when hot. Among those mentioned were magnesium chloride, sodium acid phosphate, strontium bromide, and ferric chloride<sup>64</sup>. Brookes prepares the urea adhesive in the presence of salts such as magnesium chloride, zinc sulfate, and magnesium nitrate at a pH of 5.0 to 6.5, and evaporates the resin to a dry state for subsequent use in plywood manufacture<sup>65</sup>. Sodium salts at a pH of 6 to 6.5 are described in another urea-resin patent, where the resin is evaporated to dryness<sup>66</sup>.

Substantial reduction in the hot-setting time of urea-formaldehyde resins can be obtained through the use of latent accelerators, which generate weak acids under the action of heat<sup>67</sup>. The list of accelerators includes

acetoxime benzoate, acetoxime *p*-toluene sulfonate, ethylene thiocyanate, methyl saccharin, benzoate of benzhydroxamic acid, and cyano thioformamide. Another latent catalyst of this description is hexamethylene-tetramine thiocyanate<sup>68</sup>. Betabromhydrocinnamic acid is another catalyst which liberates HBr with heat, while Howald also mentions glyceryl-phthalates yielding some free phthalic acid as a catalyst above 80°<sup>69</sup>. Very small amounts of iso-dibromsuccinic anhydride will liberate acids when heated above 100°<sup>70</sup>.

Ellis prepared a number of heat-hardenable urea-resin adhesive products with various catalysts consisting of nitrohydroxy paraffins derived from a nitroparaffin and an acyclic aldehyde. For example, in the reaction of nitroethane upon formaldehyde in the presence of an alkaline medium, 2-nitropropanol is obtained, though with twice the molar proportions of formaldehyde a nitroglycol is formed. Esters prepared from the nitro-alcohols or nitroglycols are suitable for catalysts of urea adhesives<sup>71</sup>.

In a new group of catalysts for urea resins, suited for molding compounds and adhesives, the resin is prepared by reacting two moles of formaldehyde with one of urea under alkaline conditions. It is claimed that the hardening takes place under non-acid conditions. Typical catalysts described are as follows: monochloroacetylurea, chloroacetonitrile, monochloroacetamide, monochloroacetone, and amino acetamide hydrochloride<sup>72</sup>.

Hardening under non-acid conditions or in close proximity to the neutral point has considerable advantage over strongly acid catalysts, particularly when the bonding of cellulosic materials is involved. Many of the earlier adhesive developments in urea resins would be considered undesirable in the light of modern practice, which demands a pH above 2.5<sup>73</sup>. Another technique in setting urea-formaldehyde resin adhesives is suggested in the employment of volatile acids which presumably will evaporate after they fulfill their function of setting the resin to an infusible, insoluble state. The resin is dissolved in butyl alcohol, and hydrochloric acid and formic acid are proposed as catalysts<sup>74</sup>. Typical among acids which have been added to the urea-formaldehyde resin before hardening are strong mineral acids, acetic acid, oxalic, and lactic acid; however, acid-reacting salts such as acid sodium sulfate, mono-ammonium phosphate, and aluminum chloride have been used, as well as agents which split off acids, *e.g.*, ammonium sulfate, copper sulfate, ammonium chloride, and copper chloride<sup>19</sup>.

In the development of a delayed action catalyst for urea resin adhesives, Howald employs a dry mixture of the ammonium salt of a strong acid and an ammonium salt of a substantially weaker acid<sup>75</sup>. As he points out, the advantage of the strong acid salt is to hasten the curing of the resin and the development of a strong, waterproof bond, though the useful life of the adhesive after adding the catalyst is greatly reduced. On the other

hand a weak acid salt will permit a long working life for the adhesive, though a much longer time to obtain full cure and an end product not as water-resistant as with the greater H ion concentration. By mixing the ammonium salt of a strong acid, such as ammonium chloride or sulfate as well as the ammonium salt of a weak acid such as borate or carbonate, the presence of the latter retards the acidifying of the solution to the extent that it is possible to incorporate a greater proportion of the strong acid salt than otherwise practically possible. The effect of the weaker salt wears off and cure proceeds rapidly after a period of time. Useful working life of the adhesive was prolonged as much as five times in one example. Ammonia from the strong acid salt reacts with free formaldehyde to form hexamethylenetetramine, leaving the acid radical to assist the hardening process.

In the development of another delayed-action hardener for urea-formaldehyde resin adhesives, Dearing employs a substance selected from magnesium oxide, magnesium hydroxide, zinc oxide, and zinc hydroxide<sup>76</sup>, in conjunction with an ammonium salt of a strong acid. In explaining the effect, he points out that the free formaldehyde present in solution reacts with the ammonium compound to form a hexamethylenetetramine salt which is neutralized as the oxide or hydroxide is dissolved. Thus during the initial period the acidity is neutralized until the oxide or hydroxide is consumed. More hydrogen ions continue to be generated so long as free formaldehyde is present, until the adhesive is hardened. In one example of a dry mix, 100 parts of granular urea-formaldehyde dried resin is mixed with  $\frac{1}{2}$  part of zinc oxide and 2 parts of ammonium sulfate. This mixture is stable for an indefinite period until activated by water. In this manner, the adhesive may be sold in a moisture-tight separate package, which is made ready for use on the addition of water. From a layman's point of view this has many advantages in the ease of handling.

In still another method of activating urea-resin adhesives, from 3 to 25 per cent of calcium chloride, based on the weight of the adhesive, is added to a neutral aqueous solution of urea and formaldehyde<sup>77</sup>. Cordier proposed substituted thiourea derivatives as latent accelerators for urea-formaldehyde resins, as well as ethylenediamine salts of benzoic, succinic, and like acids<sup>78</sup>. Cosgrove employed latent accelerators from benzoyl-chloride or lacthydroxamic acid for urea-formaldehyde resins<sup>79</sup>. An improvement in urea resin adhesives for plywood manufacture by reducing lumping was observed by the inclusion of tricalcium phosphate, the actual hardener being ammonium chloride or bromide<sup>80</sup>. In another specification the pH for a self-hardening urea-formaldehyde adhesive is specified as less than 4.0, with a 1 per cent aqueous solution of ammonium sulfate or phosphate<sup>81</sup>. The dry mixture is stable, though activated on addition

of water. In order to stabilize the urea-resin solution, Meiser and Howald "fixed" the free formaldehyde in the urea-formaldehyde reaction product with ammonium carbonate, the  $\text{NH}_3$  of which forms hexamethylenetetramine. By reducing the amount of free formaldehyde, the subsequent addition of ammonium chloride to harden the adhesive will not react too rapidly to reduce the working life of the adhesive<sup>82</sup> appreciably.

Powers recognized the importance of keeping volatiles to a minimum in preparing a urea-resin adhesive for cementing glass applicator rods to phenolic bottle caps. He prepared a urea resin with a pH of 5.5 to 7.0 and removed water with vacuum. The catalyst employed was 3 to 10 per cent of lactic acid. Water content of the adhesive was stated to be 20 per cent<sup>83</sup>. Salts of chloroacetic acid have also been proposed as catalysts for urea-formaldehyde resins<sup>84</sup>, as well as latent curing catalysts of N-acyl imides and N-acyl sulfonamides.

### Applications of Urea-Formaldehyde Resin Adhesives

In this country, the late 1930's gave recognition to the many advantages of urea-formaldehyde resin adhesives, and the adaptation of this material to secondary or assembly gluing operations, particularly of plywood structures, was encouraged. The availability of this material, the first synthetic-resin adhesive to be widely employed as a low-temperature curing resin, immediately offered competition to protein and animal-glue types. In a comparison of cold-setting urea-resin glues with casein glues for joints in aircraft assemblies, it was concluded that under factory conditions the urea-resin glues were capable of producing bonds whose dry strengths compared very favorably with all the principal glue joints involved in the assembly of a wooden airplane. Considering its superiority over casein in respect to water and mold resistance, its use in aircraft construction was justified<sup>85</sup>.

In a later report covering weathering exposures of unprotected plywood panels for a period of 84 months, the advantage of the phenolic-resin over the urea-resin types is readily indicated<sup>87</sup>. The phenolics compare more favorably also in data obtained for high-low relative humidity cycles and soaking-drying cycles. The superiority of phenolic-resin adhesives to straight urea-resin adhesives in water resistance is generally recognized.

Some early consideration was given to the impregnation of wood veneers with urea-formaldehyde resins in much the same manner as was conducted for phenol-formaldehyde types, though the stabilization of the wood veneers was not as successful with the urea resins as the phenolic resin impregnants<sup>88</sup>. The matter was reopened, however, when W. K. Loughborough of the Forest Products Laboratory demonstrated that wood treated with crystalline urea in aqueous solution became quite pliable and

flexible, after drying out and controlled heating<sup>89</sup>. Thick sections may be treated with warm urea solutions, and rendered quite flexible. In practical extensions of this idea, one company recommended the use of urea to prevent checking and splitting of freshly cut lumber. Urea solutions slowly diffuse into the wood to prevent checking by too rapid drying out<sup>90</sup>. In further developments the urea-impregnated wood or veneers were treated with formaldehyde to form the urea resin *in situ*<sup>91</sup>. Kassay and Williams deposited 5 per cent of urea on cellulose wood fragments<sup>92</sup>. These were dried and ground at ordinary temperatures to produce wood flour. Hall bonded wood plies with a casein-base adhesive. The plywood was then soaked in a solution of urea and formaldehyde and pressed at 3000 to 4000 psi and 300–350°F to produce a laminated wood having a very hard surface<sup>93</sup>. A special foamed glue made from a mixture of casein and urea-formaldehyde resin was used to obtain an economical spread in the manufacture of plywood. Kline described the preparation of urea resins for adhesives ("Kaurit-W") in Germany during the war<sup>94</sup>. One mole of technical urea is reacted with two moles of formaldehyde (30 per cent solution) to form a 36 per cent resin solution. This was concentrated by heating under vacuum at 65°C. Then 8 to 10 per cent of wood rye or potato flour is added to yield a mixture comprising 55 per cent resin, 10 per cent flour, and 45 per cent water. This is neutralized with sodium hydroxide to a pH of 7.0. To prepare it in powdered form, it is spray-dried to 2½ to 3 per cent moisture. A cold assembly glue is reported from the following:

"Kaurit-W"-powder, 75.7 parts  
Ground phenolic resin scrap rejects, 21.65  
Paraformaldehyde, 2.65

For maximum water resistance, resorcinol is added to the resin.

Much publicity was given by Berliner to the treatment of wood with dimethylolurea, for the purpose of hardening and strengthening it. After appropriate impregnation by the vacuum-pressure process, the resin is cured in place with heat<sup>95</sup>. In one recommended procedure 1 part of urea is dissolved to 3 parts of dimethylolurea. The solubility of dimethylolurea at room temperature is 15 to 20 per cent by weight, increasing to 50 per cent at 50°C. The stability of the resin solutions is dependent on pH. Properties as described by the manufacturer are as follows:

Dimethylolurea $\text{CO}(\text{NHCH}_2\text{OH})_2$ ,	
Molecular Weight	120.1
Melting point of 87–90% DMU,	85–90°
Melting point of pure DMU	126°
Density at 20°	1.32–1.35
pH of 10% aqueous solution	8.0–8.5

The price in quantity late in 1945 was listed at 9.0 cents per pound, which made the resin attractive from a cost standpoint. Insofar as wood stabilization was concerned, however, the superiority of the phenol-formaldehyde solutions were recognized<sup>96</sup>. Kvalnes recommended the combination of monomethylolurea and dimethylolurea for impregnating wood<sup>96a</sup>.

In reviewing some of the early successful applications of urea-formaldehyde resin adhesives, Bigelow describes the enthusiastic reception of these adhesives by the wood-working industry, because of the ability of the material to produce bonds stronger than the wood<sup>97</sup>. Applications in ski-manufacture, beer-barrel staves, boat building, and laminated plywood doors for bomb bays on aircraft are described. Hot and cold press types are

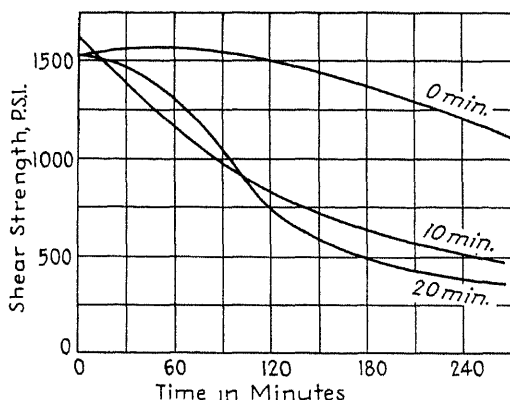


Figure 8. Characteristics of urea- $\text{CH}_2\text{O}$  adhesive on sanded phenolic laminates. Variables shown are time in minutes after adding catalyst, before adhesive is applied and three open assembly periods after application of the adhesive. All assemblies were cured 1 week at room temperature before test.

compared, with glue spreads of 30 to 40 pounds per 1000 square feet of single glue line, a spread substantially lower than for animal, vegetable or protein glues. Lower costs were achieved through the use of flour fillers. Further war-time applications are listed, particularly in bag-molding processes for resin-bonded plywood<sup>98, 99</sup>. The specific application of urea resins to the manufacture of molded plywood shapes in aircraft is described by Nebesar. He cites the use of a urea-formaldehyde resin adhesive in production operations whereby activation takes place on adding 6 parts of water to 10 of resin. The adhesive is mixed fresh every  $2\frac{1}{2}$  hours throughout the day<sup>100</sup>. Urea resin glues on wooden stressed members of car bodies have also been described<sup>101</sup>. Auxiliary fuel tanks laminated with cotton duck and urea resin have proved an excellent means of developing a structure resistant to aromatic fuels<sup>102</sup>.

In some tests in the writer's laboratory on characteristics of a typical

dry mix urea-formaldehyde resin adhesive, the strength of the glue was evaluated at different intervals after activation with water, as per manufacturer's directions. In addition, the influence of open assembly time is also shown, with data for 0, 10, and 20 mins. open assembly. The materials bonded were laminated canvas and phenol-formaldehyde plastic with sanded surfaces. Results are shown in Figures 8 and 9. These data may be compared with previous results on resorcinol-type adhesives which were tested in an identical manner. The viscosity-time curves for this thermosetting resin adhesive should also be noted. From practical experience, the use of too highly viscous glues (above a few thousand centipoises) is not to be recommended for several reasons. The first is purely mechanical: conventional glue spreaders are not prepared for handling a

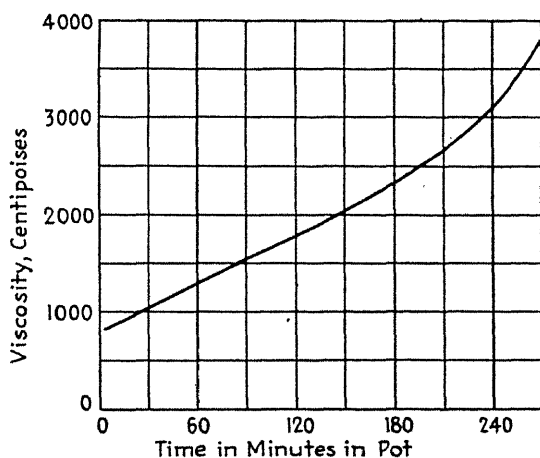


Figure 9. Viscosity stability of cold setting urea resin, after activation of catalyst

heavy, pasty material; the second is that the removal of volatiles during open assembly time proceeds much more slowly in a thicker, more viscous glue line.

In looking at important applications of urea-formaldehyde resin adhesives other than in plywood manufacture, we find an important use developing in the manufacture of corrugated fiber-board. The introduction of 5 to 15 per cent of urea resin with the starch results in minimum changes in operating conditions. The finished product is able to withstand soaking in water for several days without ply separation, whereas straight starch and silicate adhesives would fail under these conditions<sup>103</sup>.

Some interesting data on the influence of ambient temperatures on the working life and clamping time for urea-resin glues has been prepared by Stéphan and is shown in Table 11<sup>104</sup>.

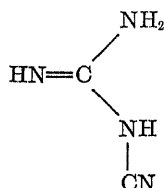
Aside from the urea-formaldehyde resin adhesives, there are other types

of aldehydes employed in the adhesive formulations, as well as other amides besides carbamide (urea). Dicyanodiamide and formaldehyde have been frequently mentioned as the base for useful adhesive products for glass and wood. Tomita describes a product of this character, preparing a dry mix

Table 11.

Prevailing Temperature (°F)	Working Life of Urea Adhesive (mins)	Clamping Time (in press) (mins)
60	360	480
65	275	395
70	220	340
75	165	285
80	125	245

for use as an adhesive<sup>105</sup>, though Wallasch first noted the possibilities as an adhesive<sup>106</sup>.

*Dicyanodiamide*

Urea and furfural have also been reacted together to form an adhesive product useful in plywood bonding. Paraformaldehyde is useful as a hardening agent for this reaction product. Colors would be dark, though for decorative plywood assemblies, where it is desired to accentuate the glue line, this may not be objectionable.

Davis prepared an adhesive for a safety glass interlayer from urea, thiourea, dicyanodiamide and formaldehyde<sup>107</sup>. Nitrocellulose was added to this combination in an organic solvent to promote toughness. The adhesive was placed on the glass plate face and then the transparent cellulose acetate sheet inserted in place, and the entire assembly cured under pressure and low heat. Ellis prepared other urea-resin adhesives also for the manufacture of safety glass<sup>108</sup>, though they did not prove as satisfactory as thermoplastic types for this purpose.

Useful adhesives and laminating varnishes have been prepared from alkylene or arylene diureas or dithioureas. Among the examples cited are ethylenediurea, 1,5-naphthylenediurea, and *o*-phenyldiurea, which are reacted with aqueous formaldehyde solution<sup>109</sup>. Amine-aldehydes, cyanamide-aldehyde, and urea-formaldehyde resin adhesives have been

used to treat rayon threads and cords employed in the manufacture of rubber tires, prior to associating the rayon cords with vulcanizable rubber<sup>110</sup>.

Acrolein has been reacted with urea to form useful adhesive products, in one example of an aldehyde other than formaldehyde<sup>111</sup>, and Novotny prepared varnishes of urea-furfural resins capable of being set with heat<sup>112</sup>. In one further example of an adhesive product which may be noted, Pollak prepared dry adhesive mixes directly from urea and hexamethylenetetramine, the reaction continuing until  $\frac{1}{2}$  mole of ammonium hydroxide was liberated<sup>113</sup>. Urea-formaldehyde resin adhesives have had minor amounts of metallic stearates included in their formulation<sup>114</sup>. Water-soluble adhesive resins have also been prepared by reaction of boric acid with equimolar proportions of biuret or ethylenediaminediuret<sup>115</sup>. Urea or thiourea is reacted with at least  $1\frac{1}{2}$  mole of formaldehyde in an acid medium in the absence of organic solvents containing OH groups. The product is treated with  $\text{NH}_3$  to make an adhesive<sup>116</sup>.

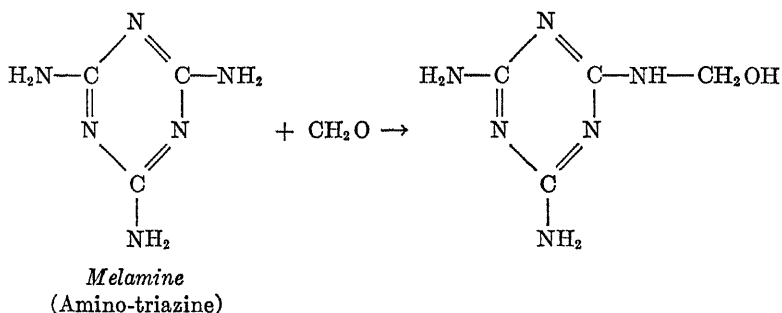
An interesting application has developed for urea resins as core sand binders<sup>117</sup>. When added in small amounts, good workability and freedom from sticking is claimed. Urea resins decompose at lower temperature than drying oils, which permits good collapsibility of the sand core.

### Melamine Formaldehyde Resin Adhesives

Considerable attention has been given in recent years to adhesives prepared from melamine formaldehyde. While chemically resembling the urea resins, the melamine resins have definite advantages in their greater resistance to water, their better heat stability, and their ability to cure or set at lower temperatures, thus requiring less pronounced hydrogen ion concentration in the catalyst. They are more expensive than the urea and phenolic resins, though their uses are expanding, particularly in combinations of the melamine with the urea-formaldehyde resins. Melamine-resin adhesives are capable of withstanding the three-hour boil test required in some government specifications, which hitherto only the phenolics have been capable of withstanding. The melamine resins have also shown considerable superiority to the ureas in various baked surface coatings<sup>118</sup>.

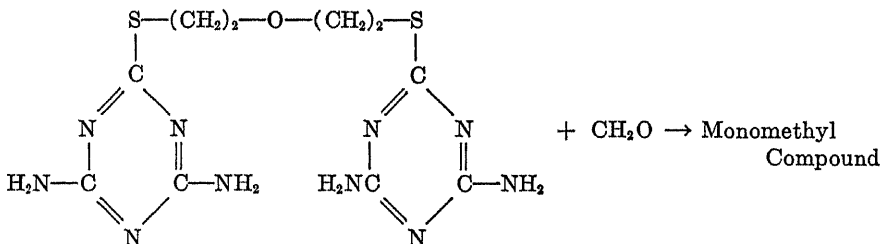
Melamine readily condenses with formaldehyde in acid or alkaline solution to form useful synthetic resins, though a considerable molar excess of formaldehyde must be present to give heat-hardenable resins. In one of the first U. S. patents on this art, Talbot claimed 2.7 to 8.8 moles of formaldehyde per mole of melamine, citing the use of various acid and alkaline catalysts<sup>119</sup>. For forming the adhesive at least 6 moles of formaldehyde are claimed in a German patent<sup>120</sup>. The preparation of dry powders by spray-drying is also mentioned. Up to six molecules of formaldehyde

may be condensed with melamine to form the hexamethylol compound, though in the example noted below, the monomethylol melamine is cited. The polyfunctionality of melamine contributes in no small measure to its stability and ease of forming thermosetting polymers:



Franklin, in 1922, seems to have been the first to heat dicyanodiamide in liquid ammonia at 90–100°, the present basis for preparing melamine<sup>121</sup>. After 1937, a number of patents on the production of melamine were issued to the Society of the Chemical Industry at Basle, and to its American affiliate, the Ciba Products Corporation. It was shown that melamine could be obtained in good quantities by heating dicyanodiamide in an autoclave with anhydrous ammonia<sup>122</sup>.

In a somewhat related problem, Bruson and Rainey prepared a large number of useful adhesives from bisthioammeline ether and formaldehyde, in conjunction with soluble blood as thickener and binder<sup>123</sup>.  $\beta, \beta'$ -bisthioammeline diethylether and formaldehyde are singled out as making good adhesives, their structural formula being represented as follows:



While melamine resins enjoyed good distribution and manufacture in this country during World War II, much of the initial work appeared abroad. Early uses as adhesives and molding compounds were brought out in a British patent, which indicated a condensation in the presence of alcohol<sup>124</sup>. Ammonium thiocyanate is also mentioned in conjunction with this development. Hardenable amino-triazine-formaldehyde condensation products, capable of hardening below 100°, were employed in the manu-

fracture of plywood<sup>125</sup>. On the other hand the melamine-formaldehyde resins were also converted to dry powders, just like some urea-resin adhesives, and were activated for use by the addition of water. Likewise, thin papers were treated with the adhesives in order to prepare thin films for bonding purposes<sup>126</sup>.

Early uses for melamine resins came in the bonding of solvent wet abrasive particles<sup>127</sup>. In a further extension of the use of melamine-formaldehyde bonding resins Swain and Light prepared abrasive particles with a mixture of 20 to 80 parts of phenol-formaldehyde and 80 to 20 parts of melamine-formaldehyde<sup>128</sup>, to form strong, heat-resistant assemblies. The usefulness of straight amino-triazine-aldehyde resin as binder was also recognized<sup>129</sup>.

Improvements to starch conversion products for adhesives were noted when melamine-formaldehyde condensation products were added. From 70 to 95 per cent of dextrin was employed and 5 to 30 per cent of melamine-aldehyde<sup>130</sup>. A dry mix prepared of this combination is activated by the addition of water. Various combinations of amino-triazine-aldehydes were observed in combination with urea and thiourea in the manufacture of adhesives. A particularly useful glue was obtained by combining them with cane sugar<sup>131</sup>.

Stable adhesive solutions have been prepared of amino di- or triazine-aldehyde resins by adding, during or after condensation, a water-soluble alkali salt of a weak organic acid. An example given is sodium acetate, with a pH less than 10<sup>132</sup>. Stable solutions of melamine-formaldehyde resins are more of a problem than with urea-aldehydes, because of the greater activity of the melamine. In consequence, the adhesives are generally distributed as dry powders in tightly sealed containers.

Other combinations of melamine-formaldehyde resins with starch and dextrin are outlined in a French patent which describes the preparation of the resin in an organic solvent. 500 parts of formalin are reacted with 126 of melamine in the presence of 300 parts of ethyl alcohol until the melamine enters solution. Three parts of the melamine resin are combined with 7 parts of dextrin to form a good, hot-setting adhesive for plywood<sup>133</sup>. In still another development, melamine-formaldehyde resins (5 to 30 per cent) and dextrin (70 to 95 per cent) were combined with ammonium chloride to form a dry adhesive which could be activated with water<sup>134</sup>. Widmer and Fisch assigned patents on the developments of amino-triazine binding agents to Ciba Products Co. in 1943, citing some for combinations with starch. In a typical example of their practice, 63 parts of melamine are dissolved with stirring into 170 parts of an aqueous solution of 32 per cent formaldehyde. The combination is neutralized and chilled; after standing overnight the solution, which has solidified to a white mass, is

broken up and dried in a current of warm air<sup>135</sup>. Combinations of melamine resins with starch are cited in their claims. Widmer and Fisch also prepared melamine-resin adhesives by reacting 1 mole of melamine with 5 moles of formaldehyde in an alcoholic solution in the presence of 0.01 mole of hydrochloric acid<sup>136</sup>. They also present additional claims of melamine-aniline-formaldehyde adhesive products, and melamine-urea-formaldehyde condensation products.

Aside from the general use of melamine-formaldehyde resin adhesives, melamine has been added directly to heat-hardenable urea-formaldehyde resins as an accelerator of hardening. Brookes specifies 2 to 20 per cent melamine for this purpose<sup>137</sup>. Seperski likewise called attention to the use of melamine in urea-formaldehyde resins to lessen their acidity and increase their waterproofness<sup>138</sup>.

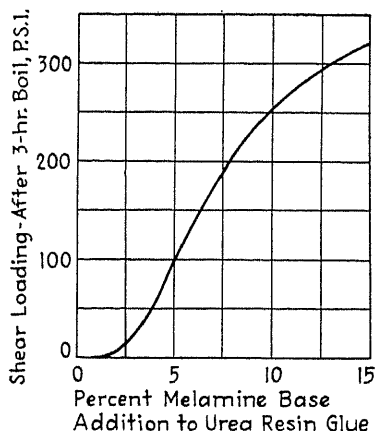


Figure 10.

Influence of melamine on plywood strip shear test of urea adhesive.

In reviewing the melamine-urea-formaldehyde resins, McHale describes various forms of these adhesives. Low bag-molding temperatures of 105 to 125° are possible with these resins in developing curved plywood shapes, though with 0.5 per cent ammonium chloride as catalyst it is possible to have room-temperature setting. In Figure 10 the influence of small percentages of melamine on the properties of urea-resin adhesives is reproduced from McHale's paper<sup>139</sup>.

Phenol-melamine-formaldehyde resin adhesives have also been prepared. Amino di- or triazines are condensed with formaldehyde in the presence of phenolic bodies capable of reacting with formaldehyde<sup>140</sup>. Starch is also mentioned as a filler addition. D'Alelio has done considerable work on the development of reaction products of diazines and their derivatives with aldehydes<sup>141-145</sup>. The heat-convertible resinous condensation products described by D'Alelio are recommended for general adhesive applica-

tions. A large number of bis (diazinyl thio alkylamido) and bis (diazinyl thio alkylthioamide) derivatives of divalent hydrocarbons which are employed in making the condensation products are listed. Specific attention is directed to the use of urea or melamine as modifiers for the diazine derivatives<sup>141</sup>. Both acid and alkaline catalysts are employed. The thermoplastic condensation products which may be formed are useful as plasticizers for other synthetic resins, while the thermosetting materials are employed in molding, laminating, and adhesive formulations.

D'Alelio also developed molding, laminating, and adhesive materials from triazines<sup>146, 147</sup>. In a typical example, 143 parts of melamine are reacted with 245 parts of 37 per cent solution of formaldehyde and sodium hydroxide until a clear syrup is formed. On mixing with 1 to 2 per cent of  $\alpha, \beta$ -dichloropropionamide, an infusible, insoluble mass is formed. The patents also claim a process of partially condensing an aliphatic aldehyde with a phenol and reacting the same with 2 to 20 per cent of melamine.

Ripper prepared intermediate condensation products of dicyandiamide and melamine in a molar ratio of 8 to 1 and 4 to 1 with formaldehyde under alkaline conditions<sup>148</sup>. The materials are heated at 50° until a creamy, water-dispersible resin is formed which is suitable for adhesives and laminating. In England, Bloxam prepared melamine-formaldehyde resins suitable for plywood adhesives<sup>149</sup>. DeBruyne and Hubbard also prepared plywood adhesives from melamine, urea, or thiourea resin and a foam hardener of 10 per cent ammonium chloride, 10 per cent saponin, and 80 per cent water<sup>150</sup>.

Melamine-formaldehyde resins can well fulfill the simultaneous role of an impregnating as well as an adhesive agent. Of clear, water-white consistency they are successfully employed in the development of laminates containing colored, decorative exterior patterns. For example, thin printed papers or sheets of colored cloth may be impregnated with say 50 to 60 per cent of melamine-formaldehyde resin from a 50 per cent aqueous solution and successfully bonded to the outside surfaces of plywood. A few examples of these products are illustrated in Figure 11. In its role as an impregnant and adhesive, melamine-formaldehyde insures the development of a hard, scratch-resistant, water-repellant surface which is quite durable. The plywood may have the outside sheet bonded in place at the time of manufacture in the hot press, or else the resin-impregnated layer may be cemented on in a separate operation. The developments of these exterior water-repellant and decorative faces for plywood will do much to increase the popularity of plastic-faced plywood in the home and office. Stronger in impact strength and lower in cost than a solid sheet of plastic, combinations of thin resin-impregnated sheets as exterior faces with plywood cores will provide a large outlet for plastics in the field of building materials.

Among other noteworthy uses of melamine resins is its application as a low-pressure laminating resin. Glass laminates prepared by Delmonte with the aid of melamine-resin adhesives provided contoured surfaces at relatively low tool costs at low temperatures with the proper type catalyst<sup>151</sup>. In this technique, the melamine resin served as an impregnant as well as a binder, though plaster of paris was employed as a partial filler in conjunction with the melamine. Excellent heat resistance was obtained in such combinations. Melamine formaldehyde-glass cloth laminates

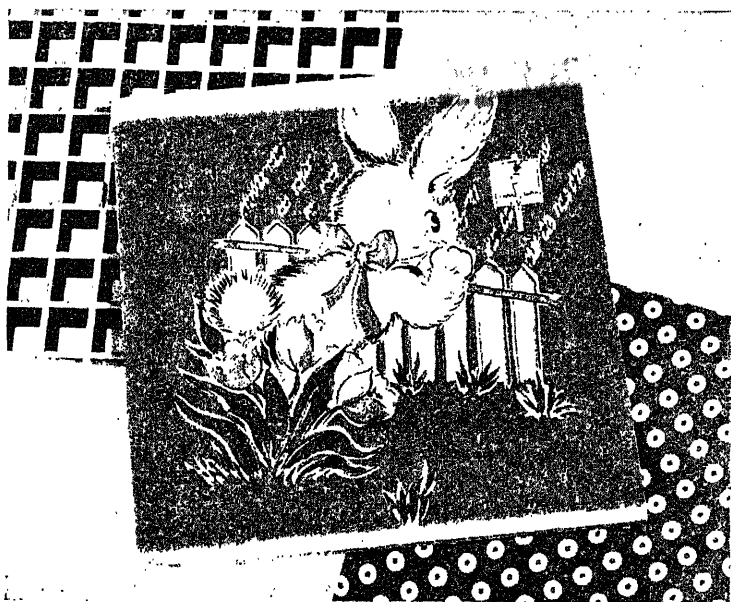


Figure 11. Melamine resin impregnated cloth overlays applied to surfaces of plywood

possess the best fire and heat resistance of molded and laminated organic plastics. They may be excelled in these respects by silicone resins.

Melamine-formaldehyde resins as impregnants for papers and textiles have rendered an invaluable service in improving the qualities of these materials. Not very large quantities have been needed; generally a few per cent has been sufficient to increase greatly the wet strength of the paper and to stabilize the textile products against shrinkage. For example, Hofferbert applied 0.5 to 5.0 per cent of melamine-formaldehyde resin to paper stock to obtain a product of high wet strength<sup>152</sup>. Additions of the melamine resin are generally made to the wet pulp in the beater. The usual paper sizing materials may also be present<sup>153</sup>.

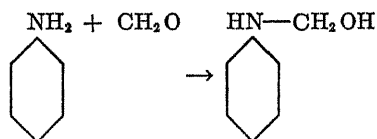
A reduction in the felting and shrinking of wool can be accomplished with unpolymerized alkylated methylol melamine-formaldehyde condensation

products. From 2.5–15 per cent is applied to dry wool and heated to 100–150° to insolubilize<sup>154</sup>. Beer also developed shrink-proof textiles with the aid of urea and thiourea-formaldehyde<sup>155</sup>. Crease-proofing of textile products has been known for some time; it is accomplished by impregnating the cotton fibers with urea-formaldehyde resins. The textile and paper industries are relying on these impregnating resins more than ever before. Some of their characteristics as impregnants and adhesives for paper and textile products are covered in a later chapter.

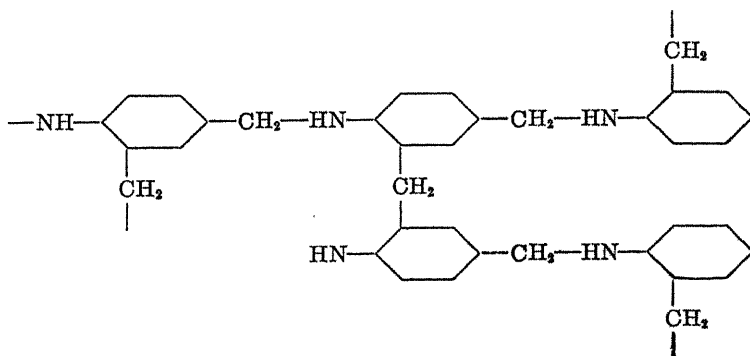
### Aniline-Formaldehyde Resins

The condensation products of aniline-formaldehyde have found some uses as adhesive materials, both alone and in combination with other resins. In the chapter on phenolic resins, attention was directed to certain developments in Great Britain involving the combination of aniline-formaldehyde with phenol-formaldehyde as an adhesive for bonding together various types of plastics<sup>156</sup>. The aniline-formaldehyde resins were prepared with 2 moles of formaldehyde to one of aniline. Resin-like polymers are formed, according to Bohler, on heating anhydroformaldehyde-aniline ( $C_6H_5N=CH_2$ ), the aniline residues being linked through the nitrogen atoms and  $CH_2$  bridges<sup>157</sup>. Condensation of aniline with more than one mole of formaldehyde under acid conditions, followed by neutralization and drying, is said to yield dense, moldable products<sup>158</sup>.

The general reactions to form the aniline-formaldehyde resins may be indicated in the following manner:



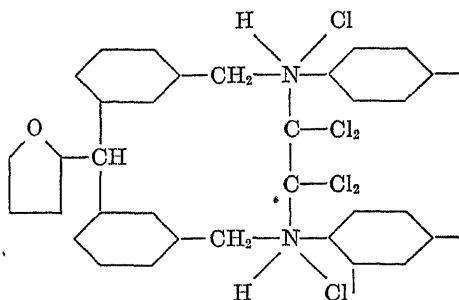
Frey suggests the following network structure to represent the infusible, insoluble polymer which may be formed<sup>159</sup>:



Commercial laminates of aniline-formaldehyde bonded paper and cloth are available. They are generally characterized by a reddish-brown coloration. Their outstanding qualities appear to be good electrical properties.

Useful addition agents have been prepared from other aldehydes than formaldehyde in reaction with aniline. For example, a butyraldehyde aniline condensation product is described as a good accelerator for adhesives prepared from chloroprene<sup>160</sup> and other synthetic resins. Likewise, the presence of aniline-furfural condensation products contribute to the good molding properties of lignin plastics<sup>161</sup>.

Aniline-formaldehyde resins have been developed to cement abrasives such as aluminum oxide, in the manufacture of grinding wheels. Kistler shows numerous reactions of aniline with formaldehyde and furfuraldehyde. In some instances, he specifies the reaction in presence of halogenated, substituted paraffinic compounds such as hexachloroethane, tetrachloropentane, and beta butylene bromide, indicating cross-linking of the polymer as follows<sup>162</sup>:



An advantage is claimed in grinding operations whereby traces of acid liberated by the resin bond prevents the metal from sticking to the abrasive grains. A greater amount of metal will be ground for a given wheel wear with this type of resin binder than with a shellac or phenolic-resin bonded wheel. Chlorinated polymers, such as polyvinyl chloride, rubber hydrochloride, chlorinated rubber, chlorinated polyisobutylene, and polyvinylidene chloride are combined with a condensation product of aniline and one to three moles of formaldehyde or furfural, to give the same effect as the halogenated paraffin<sup>163</sup>. Chlorohydrins, bromohydrins, and iodohydrins, such as ethylene bromohydrin, ethylene chlorohydrin, beta-butylene chlorohydrin, alpha-butylene chlorohydrin, 2,3-amylene chlorohydrin, and others, are also combined with aniline-formaldehyde condensation products to cement the abrasives. Cross-linking of polymers with these addition agents is claimed<sup>164</sup>. Melamine mono-, di-, and trihydrochloride in combination with aniline-formaldehyde<sup>165</sup> and halogenated fatty oil acids and

their esters are also mentioned<sup>166</sup>. Another abrasive binder is prepared from the simultaneous condensation of melamine-aniline and formaldehyde in the presence of a strong acid catalyst<sup>167</sup>.

In general, it should be noted however, that no commercial adhesives are at present prepared solely from aniline-formaldehyde. The polymers from this reaction tend to be more friable than the phenolics or urea-aldehydes already discussed. Their usefulness, however, appears in the employment of the material in conjunction with other polymers. Of interest as a catalyst however, is aniline hydrochloride,  $C_6H_5NH_2 \cdot HCl$ , which may under certain conditions liberate  $HCl$  to activate other types of thermosetting resin adhesives. It may also be noted that paraformaldehyde-aniline condensation products have been suggested for adhesives<sup>168</sup>. As an adhesive for insecticides, furfural is condensed with aromatic amines of the group of aniline, *p*-toluidine, and beta-naphthylamine<sup>169</sup>.

### Sulfonamide-Aldehydes in Adhesives

Developments in sulfonamide-aldehyde resins have largely centered upon *p*-toluene sulfonamide, a by-product in the manufacture of saccharin. *p*-Toluene sulfonamide ( $CH_3C_6H_4SO_2NH_2$ ) and a large number of sulfonamides were discovered to be capable of reacting with formaldehyde to form a number of useful semi-solid or hard thermoplastic resins<sup>170</sup>. They are available commercially in this country in the form of a viscous liquid, soft resin, and hard, brittle products<sup>171</sup>. When heated, *p*-toluene sulfonamide formaldehyde resins give off a small amount of formaldehyde. Their presence in cellulose acetate formulations tends to increase the retentivity of plasticizers by preventing their exudation. Films prepared from cellulose nitrate are much harder in the presence of these resins.

Among the early uses of these materials were adhesive applications in automobile safety glass for cementing the cellulose acetate or nitrate sheet between the sheets of plate glass. Dreyfus prepared a resin from benzene-sulfonamide-aldehyde which he combined with cellulose acetate or cellulose ether to form the adhesives<sup>172</sup>. Toluene and xylene sulfonamide, condensed with formaldehyde or furfural, are also employed as adhesives in safety glass manufacture<sup>173</sup>. The cementing of cellulose nitrate to glass was facilitated by cellulose nitrate dope plus toluene sulfonamide-formaldehyde, camphor, and tricresyl phosphate<sup>174</sup>. Gardner also employed sulfonamide-formaldehyde resin in conjunction with cellulose esters as adhesives for safety glass. One typical cement he described included nitrocellulose (25 parts), butyl acetate (75 parts), *p*-toluene sulfonamide formaldehyde (50 parts) and toluene (50 parts)<sup>175</sup>. Moss used films of toluene or ethyl-toluene sulfonamide-aldehyde resin to bond cellulose acetate to sheets of glass to render them shatter-proof<sup>176</sup>.

In other modifications, resins compatible with cellulose esters and cellulose ethers were prepared by condensing sulfonamides of aromatic ethers with aldehydes. These showed promise as adhesives and plasticizers<sup>177</sup>. The heat-sealing qualities of these resins were recognized in combination with cellulose nitrate and alkyd resins by Edgar<sup>178</sup>. Similar combinations were described in a U. S. Patent<sup>179</sup>.

In a study of the plasticizing effect of sulfonamides on cellulose acetate, Carswell determined that the resinous substance from *p*-toluene sulfonamide-formaldehyde was superior to the sulfonamides not combined with formaldehyde. The comparison was made on the basis of color retentivity, weather resistance, tensile strength, and light-fastness<sup>180</sup>. McMaster and Cooper made a study of the water-soluble properties of these resins<sup>181</sup>.

Table 12. Solubility and Miscibility of Aryl-Sulfonamide Formaldehyde Resins.

Material	Effect	
Alcohol	Soluble	Films generally remain wet or tacky
Ketones	Soluble	Films dry hard
Esters	Soluble	Films dry hard
Aromatic hydrocarbons	Soluble	Films dry hard
Aliphatic hydrocarbons	Insoluble	
Fatty acids	Miscible	
Drying oils	Not miscible	
Vinyl resins	Miscible	
Shellac	Miscible	
Carnauba wax	Not miscible	
Paraffin	Not miscible	

A pressure-sealing, normally tacky adhesive cellulosic sheet was prepared with the aid of *p*-toluene sulfonamide-formaldehyde resin, polyvinyl acetate, and dibutyl phthalate. This adhesive layer was bonded to the cellulosic sheet<sup>182</sup>.

The selection of the sulfonamide-formaldehyde resin for adhesive purposes is determined by the qualities that are to be brought out in the adhesive. Permanent softness and tackiness is imparted by the softer grades, which are quite sticky resins, while hardness may be derived from the more brittle grades. The availability of some free formaldehyde, particularly upon heating, adapts these resins to chemical combination with some of the more active resinifying materials, such as resorcinol, though in practice the latter would be partially polymerized in combination with some aldehyde. The writer has observed increased adhesiveness on the part of phenolic resin adhesives plasticized with near molar quantities of sulfonamide-formaldehyde resins.

The gasoline resistance of the sulfonamide-aldehyde resins should make them of potential interest to adhesive applications in gasoline tanks and related equipment. They are not miscible with drying oils and waxes, but are miscible with various other substances such as in Table 12<sup>171</sup>.

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## Chapter 4

### Miscellaneous Thermosetting Resin Adhesives

There are numerous miscellaneous thermosetting-resin adhesives which have not as yet attained the large volumes of applications enjoyed by the phenolic, resorcinol, urea, or melamine resin adhesives. From the data available on these miscellaneous resins it is possible to find noteworthy contributions to the art of developing adhesion between materials. In particular, resins such as the alkyds, furfurals, styrene polyesters, some of the silicones, polyurethanes and unsaturated alkyds will be reviewed and their utilization as adhesives discussed. To avoid too much separation of the alkyd resin groups, some of the thermoplastic polymers, such as the maleic anhydride "adducts," will be included in this chapter. Thermoplastic silicone and polyurethane types will also be introduced.

In examining the majority of the thermosetting-resin adhesives one gains the impression that the good adhesive properties arise more by accident than by intent. In bonding cellulosic materials like paper and wood, the problems are not too acute, inasmuch as there is a large number of adhesive agents whose strength characteristics are appreciably greater than the relatively weak shear properties of the cellulosic products. On the other hand, when adhesives are proposed for the more ambitious attempts to cement solid organic plastics, ceramics, and metals, a closer examination of fundamentals should be undertaken. It must be remembered that the range of molecular weights in a typical organic plastic includes low and high molecular weight fractions, and that the presence of unreacted portions in the typical thermoplastic polymer or partially reacted thermosetting resin will influence the adhesive effect. One may consider that the specific adhesion properties are due to the lower molecular weight fractions or side chains, and that the cohesive properties of the film formed are due to the higher molecular weight portions. With some justification then it is possible to examine the potential usefulness of raw materials for synthetic-resin adhesives by their effect on the surfaces to be bonded, that is to say, the effect of the partial polymer or unpolymerized constituents. Good wetting properties and evidence of chemical affinity are two of the criteria which will indicate the probable behavior of the low molecular weight and unreacted fractions in the normal resin adhesive.

Analysis of the theory of adhesion, which will be dealt with in greater detail in chapters to follow, should be predicated not upon the probable behavior of an average molecular weight of a given high polymer, but rather upon a heterogeneous family, possessing portions having chemical similarity, as well as components capable of developing bonds to materials on other surfaces.

### Resin Adhesives from Polyhydric Alcohols and Polybasic Acids

The condensation of polyhydric alcohols with polybasic acids has led to the development of a number of commercial resins which run close to the phenolics in the tonnage produced. Their greatest field of utilization has been as modified forms in combination with various drying oils, with innumerable applications as surface coatings. The requirements of this industry have been so large that relatively little attention has been paid to the adhesive field. However, there are certain elements of these developments which are of potential interest to this field. Of the various polyhydric alcohols employed in the manufacture of alkyd resins or polyester resins, glycerin has been the most important, with other alcohols, *e.g.*, ethylene glycol and pentaerythritol, also figuring prominently in the materials produced.

Among the dibasic acids most frequently employed in the development of the polyester resins are phthalic acid and maleic anhydride. Others which are also growing in importance are diglycollic, fumaric, sebacic, adipic, and succinic acids.

Most of the research on the structure of the polyester or alkyd resins has been devoted to the reactions of glycerin with phthalic anhydride. While some investigators hold the opinion that the flexibility of the alkyd resins is due to the presence of long-chain molecules<sup>1</sup>, others believe that the condensation products of glycerin and phthalic acid, which form spherocolloids comparable to the phenol-formaldehyde resins, owe their flexibility to a low degree of polymerization<sup>2</sup>, and that substantial quantities of low polymerized materials act as a swelling medium for the higher polymers. The progress of the condensation reaction can be readily followed by titration of the free acid reagents present. Kienle and associates observed that at the beginning of the reaction there was a very rapid drop in the amount of free acid present; but the disappearance of the free acid then became quite slow, continuing so until an infusible gel resulted<sup>3</sup>. In practice, the average degree of polymerization is probably not greater than 6 or 8 units, when gelation sets in<sup>4</sup>. Kienle, in his work on the condensation products of polybasic acids and polyhydric alcohols, established some useful postulates based on the polyfunctionality of the reactants<sup>5</sup>:

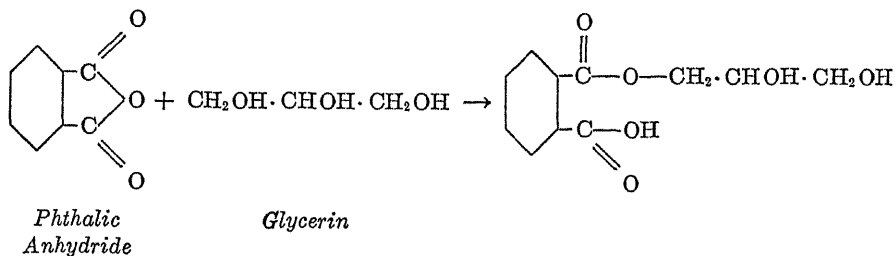
(1) Organic compounds of high molecular weight are formed when the interacting molecules are poly-reactive.

(2) Interlinking of molecules proceeds according to the chance contact of any two reactive points.

(3) Relative size and shape of the reacting molecules and the position of the reactive points largely determine the physical properties of the resulting polymer, such as hardness, flexibility, heat convertibility, etc.

It is also significant, as Kienle brought out, that when there are more than two reactive points on one molecule and at least two such points on another, a thermosetting structure is formed. On the other hand, the simplest additive polymer, forming a thermoplastic, consists of a 2,2-polymer.

Phthalic acid reacts readily with glycerin at 200°. Esterification takes place rapidly, with the formation of acid phthalate esters:



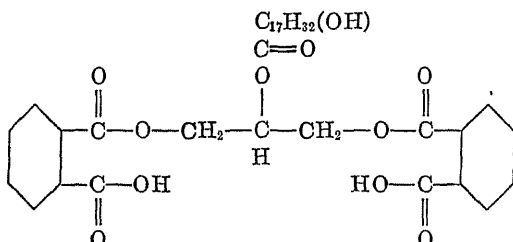
Fairly high temperatures are required to attain the infusible, insoluble state, because the rate of cure is not as rapid as for urea and phenolic resin types. The usefulness of the alkyd resins, however, has been made possible by appropriate modification with monobasic fatty acids, which are capable of saturating one of the functional points on glycerin. This prevents early gelation and also makes the resins compatible with various oils and plasticizers.

A good description of the preparation of the alkyd resins and modification with fatty acids or drying oils is contained in one of Kienle's early patents, which illustrates the general procedure<sup>6</sup>:

"About 92 parts by weight of glycerin and 296 parts by weight of phthalic anhydride are heated with the temperature gradually rising. At 160° a clear, straw-colored solution is produced. The temperature is gradually increased to 200°, water vapor and some anhydride being given off. At this point an additional quantity of phthalic anhydride (say 74 parts by weight) and 140 parts of one or more fatty acids derived from a drying oil, such as chinawood, linseed, or perilla. Heating is continued in a temperature range of 190–210° until frothing and the giving off of vapors ceases and a clear liquid is formed."

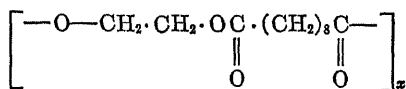
Instead of mixed acids from drying oils, oxidizable unsaturated acids such as elaeostearic acid, linoleic, or linolenic acid may be employed, as

well as the saturated fatty acids. The probable reaction of a fatty acid upon a free alcohol group in glycerin may be illustrated below by the action of ricinoleic acid ( $C_{17}H_{32} \cdot OH \cdot COOH$ ) upon the glyceryl phthalate:



Cross-linking of the polymers may take place through the points of unsaturation in the fatty acid groups. Air-drying or baking of films prepared from these materials hastens the cross-linking and polymerization processes.

Carothers has given considerable attention to the development of polyester resins of relatively high molecular weight and the principles underlying ring and polymer formation<sup>7</sup>. A large variety of useful products can be prepared from polyester resins, including not only the thermosetting types but also the thermoplastic derivatives, which may function as plasticizers for other synthetic resins or cellulose derivatives. In fact, viscous derivatives possessing good tackiness may be prepared from some of these. Non-rigid elastomers may be prepared from dibasic acids and dihydric alcohols. For example, adipic acid or sebacic acid reacted with ethylene glycol yields a rubber-like elastomer ("Paracon", "Paraplex 100"). These elastomers may serve as plasticizers or bases for adhesive products. The introduction of a minor proportion of a component with three or more reactive positions will result in a cross-linked structure with better solvent resistance and less creep under stress. Trihydroxy compounds such as trimethylolpropane and polyisocyanates such as hexanediisocyanate have served as cross-linking reagents. The reaction between ethylene glycol and sebacic acid is



*Glycol-sebacate*

In an analysis of the development of synthetic resins from polyhydric alcohols and polybasic acids, Bevan pointed out four stages<sup>8</sup>:

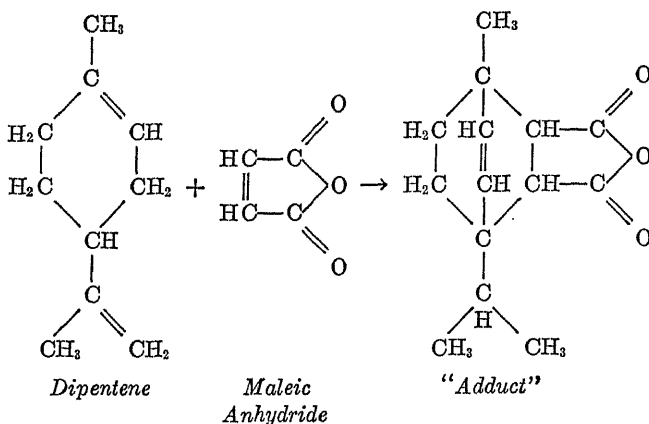
1. *First Period.* This was marked by the random production of resinous substances from polybasic acids and polyhydric alcohols. The work

of W. Smith on glyceryl phthalates was noteworthy, however. The use of this resin as a cement was suggested<sup>9</sup>.

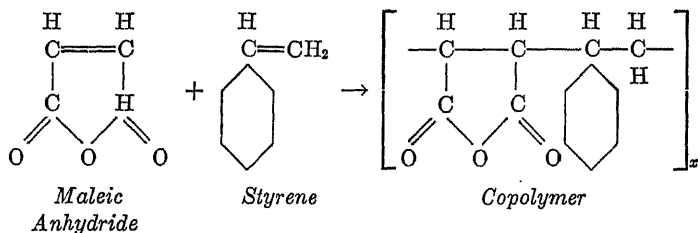
2. *Second Period.* A number of patents by General Electric Company and the Barrett Company, commencing in 1913, covered uses for the phthalic anhydride, then being produced at relatively low cost. During this period Arsem proposed the replacement of part of the phthalic acid by its molar equivalent of oleic acid<sup>10</sup>. Various dibasic acids were explored and cited in the patents, which called attention to the value of the alkyd resins as baking varnishes and impregnants.

3. *Third Period.* Immediately after World War I there was renewed activity in the alkyds. Weisburg defined the stages of the resinification process as (a) fusible, soluble, affected by water; (b) fusible, insoluble, affected by water; and (c) infusible and insoluble, unaffected by water<sup>11</sup>. This period was further marked in the early 1930's by the combinations of drying oils with alkyd resins. By heating fatty acids with the polyesters, Kienle contributed to the "fatty acid process"<sup>12</sup> of modifying the alkyds. "Fatty acid-fatty oil" combinations were commercially significant because, by condensing the polyhydric alcohol and polybasic acid in the presence of various monocarboxylic acids, followed by drying oils, a wide range of properties was obtained<sup>13</sup>. In the presence of traces of water at high temperatures, oil is continuously hydrolyzed to free fatty acids which combine in the alkyd resin being formed<sup>13</sup>. In still another process a partial ester of the polyhydric alcohol and monobasic fatty acid is formed, which subsequently esterifies with a polybasic acid<sup>14</sup>. Finally, the combination of the polyhydric alcohol, polybasic acid, and drying oil was effected in the presence of mutual solvents in the "solvent process". Aliphatic alcohols<sup>15</sup> and xylene<sup>16</sup> are typical.

4. *Fourth Period.* This period is marked by refinements in polyester resins and recognition of the fact that the homogeneity of the resins formed from polyhydric alcohols and polybasic acids is dependent upon the water-solubility of the acids. The replacement of phthalic anhydride by maleic anhydride also resulted in some noteworthy advances. Saunders obtained a resin from unsaturated polybasic acids such as maleic anhydride and polyhydric alcohols, which was catalyzed by benzoyl peroxide<sup>17</sup>. Another development of this fourth period is the Diels-Alder synthesis involving maleic anhydride and conjugated dienes<sup>18</sup>. Of particular importance to the field of synthetic-resin adhesives are the ethylene glycol, diethylene glycol, and triethylene glycol esters of the "adducts" of maleic acid or anhydride with a terpene, such as terpinene, terpineol, dipentene, pinene, etc.<sup>19, 20</sup>. Even though some of the monocyclic terpene hydrocarbons are not conjugated dienes, they too react to form "adducts" with maleic anhydride as follows:



The alpha-beta enal grouping ( $-\text{C}=\text{C}-\text{C}=\text{O}$ ) important to the Diels-Alder synthesis may be in a straight chain (acrolein, acrylic acid, crotonaldehyde) or in a ring (quinone, maleic anhydride, itaconic anhydride, or citraconic anhydride) as pointed out by Ellis<sup>21</sup>. Investigations of the reactions of both alpha-phellandrene and alpha-terpinene show that definite amounts of polymeric products were obtained in addition to the monomeric cyclic derivatives. The polymers as well as the monomers were observed to have an anhydride structure<sup>22</sup>. A polymeric anhydride structure has also been obtained in the reaction between styrene and maleic anhydride, though an additive rather than Diels-Alder reaction is claimed<sup>23</sup>; this reaction is effected in the presence of ultraviolet light. A number of resins may be obtained which appear to have potentially useful adhesive properties. In further reactions, these resins are prepared for coatings by esterifying some of the carboxyl groups with monohydroxy alcoholic esters of a polyhydric alcohol and fatty acid<sup>24</sup>.



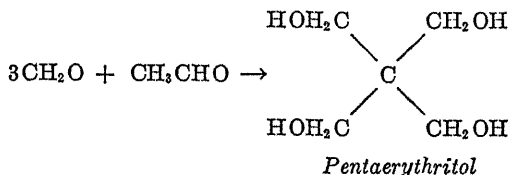
The various "adducts" prepared from maleic anhydride are employed in the manufacture of alkyd or polyester resins by further reactions with glycerin and drying oils, following methods already reviewed. Better spirit solubility and oil solubility are claimed for these resins over the corresponding phthalic anhydride types. These "adducts" represent an important starting point for the preparation of useful adhesives.

In a study of the various adhesives prepared from the glycol esters of terpene maleic anhydride, Long reports the following proportions to be particularly effective<sup>20</sup> as adhesives:

Ethylene Glycol Ester of Terpene-Maleic Anhydride	Diethylene Glycol Ester of Terpene-Maleic Anhydride	Triethylene Glycol Ester of Terpene-Maleic Anhydride
10%	30-50%	to total 100%
15%	25-50%	Ditto
20%	25-45%	Ditto
25%	25-35%	Ditto

As Powers points out, the reaction of abietic acid in wood rosin with maleic anhydride leads to the formation of tribasic acid anhydrides used in polyester resins for varnishes<sup>25</sup>. In further studies involving wood rosin acids in adhesive formulations, and unsaturated polycarboxylic acids, the "adduct" formation should be kept in mind.

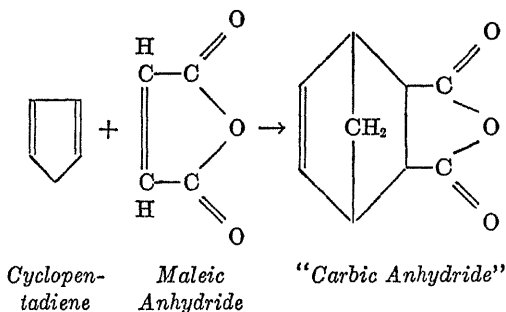
Pentaerythritol, prepared from the reaction of acetaldehyde and formaldehyde in a mild alkaline solution, is more reactive than other polyhydric alcohols such as glycerol, mannitol, or sorbitol in the preparation of alkyd resins from phthalic anhydride.



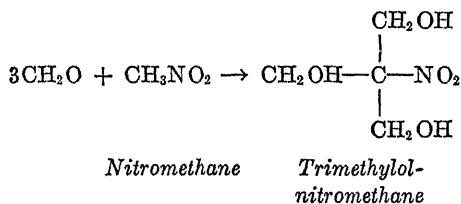
More recently the success of the technical pentaerythritol in surface coatings has been attributed to the presence of the dimer impurity formed as by-product in above reaction. Burrell has shown the superior films and drying properties of polypentaerythritols<sup>26</sup>. Mixed esters of polypentaerythritol and pentaerythritol have been shown to be useful plasticizers for cellulose derivatives and synthetic resins<sup>27</sup>. During World War II, the restrictions applied to glycerine and phthalic acid, due to shortages of raw materials<sup>28</sup>, encouraged developments in other types of polyester resins. Pentaerythritol helped to alleviate this situation.

The reaction of maleic anhydride upon cyclopentadiene to form 3,6-endomethylene-Δ-4-tetrahydrophthalic anhydride, known commercially as "Carbic anhydride", plays an important role in the formation of adhesives for steel motor laminations in motor construction<sup>29</sup>. This "adduct" is in turn reacted with glycerin, or mixtures of ethylene glycol and pentaerythritol, to obtain between 2 to 3 hydroxyl groups per molecule, and hence a thermosetting polymer. This in turn is combined with an alkyd resin prepared by cooking 2 moles of maleic anhydride with one mole of pentaerythritol at 120 to 130° for three hours. The final specification

states an adhesive composition of 10 to 50 per cent polyvinyl acetate, plus 50 to 90 per cent of a resinous material from polyhydric alcohol and 3,6-endomethylene- $\Delta$ -4-tetrahydrophthalic acid and polyhydric alcohol and a minor proportion of maleic anhydride-pentaerythritol. The blends of these three resinous materials are soluble in alcohol. In addition to steel, glass fiber sheets and mica flakes are bonded with this adhesive composition.



Among other polyhydric alcohols from which polyester resins may be formed, as well as useful adhesive products, is trimethylolnitromethane. The writer has obtained some interesting adhesive products through polymerization products of trimethylolnitromethane. The alcohol, however, can be condensed with polybasic acids to form an alkyd type resin. The reaction of formaldehyde with nitromethane is best carried out under mild alkaline conditions:



Trimethylolpropane, prepared from nitropropane, has served as a cross-linking agent for linear polyesters. Among other polyhydric alcohols which are promising for adhesives as well as coatings, both because of their individual physical characteristics as well as resin-forming abilities, are the polyethylene glycols,  $\text{CH}_2\text{OH} \cdot (\text{CH}_2-\text{O}-\text{CH}_2)_x \text{CH}_2\text{OH}$ . While they are unctuous compounds, they are water-soluble, ranging up to 6000 in molecular weight<sup>80</sup>. The higher molecular weight varieties are wax-like solids, though the lower molecular weight compounds are liquids. Freezing points range from 0 to 60°. This whole series of compounds should prove most interesting from the standpoint of synthesis of high polymers with special adhesive properties. The presence of hydroxy groups at end

of chains makes the material chemically reactive. Preparation of the polyethylene glycols has been studied by Staudinger<sup>31</sup> and by Hibbert<sup>32</sup>. Carothers prepared numerous alkylene esters of polybasic acids through processes of esterification, and outlined various examples<sup>33</sup>. The polyethylene glycols have been suggested as plasticizers for polyvinyl alcohol<sup>33a</sup>.

### Unsaturated Polyesters

Since the beginning of World War II there has been considerable development work upon polyester resins from unsaturated alcohols and unsaturated acids, leading to the formation of what have been called unsaturated alkyd or polyester resins. A special group of unsaturated polyesters is formed from allyl alcohol which has only one hydroxyl grouping. Polymerization of these compounds has depended upon opening of the double bond, rather than condensation-polymerization processes described in preceding paragraphs. The products which have been prepared with the aid of these resins have largely been laminated cloth and woven glass fibers, known to the plastics industry as low-pressure laminates<sup>34</sup>. These laminates have attracted considerable attention because in combinations with low-density balsa cores, they have offered structural materials competitive to light weight, high-strength aluminum alloys. They are known as low-pressure laminating resins, because they are relatively low in viscosity at the time of application, contain negligible volatile material, and will bind the layers of cloth or glass fibers together in a relatively short time with the aid of heat and pressure, forming an infusible, insoluble structure. Among other applications are the manufacture of transparent thermosetting plastic sheets<sup>35 36</sup>.

The polyester resins are generally polymerized with the aid of catalysts in combination with heat or exposure to ultra-violet light. This is generally accompanied by an appreciable amount of volumetric shrinkage, averaging 10 to 15%, though final properties are modified somewhat by the inclusion of a partial thermoplastic polymer. Partially polymerized styrene or vinyl acetate usually fill the latter category. In the preparation of the low pressure laminates, curing is usually conducted out of contact with air, the entire assembly being encased within a cellophane or polyvinyl alcohol bag. The cured products display a remarkable tenacity for smooth surfaces of wood or glass and hence some release agents are necessary. Regenerated cellulose or water soluble cellulose ethers may be employed for that purpose.

While the role of these polyester resins is largely that of a binding agent, where they fulfill the dual role of cement and impregnant, the possibilities have not been commercially explored as a miscellaneous cementing agent between non-porous and semi-porous materials. From their performance it is safe to predict important roles in this function. For example, in

preparing some flat low-pressure laminates on the surface of plate glass, if a release agent or undersheet of regenerated cellulose is not present, some of these polyester resins will establish a bond to the glass sheet which is stronger than the glass sheet itself.

From the standpoint of adhesive theories, it is rather interesting to note the influence of very fine flock fibers on the bonding characteristics of some of the polyester resins. There was a very great improvement in inter-laminar strength on the addition of a few per cent of fibers<sup>37</sup>. Figure

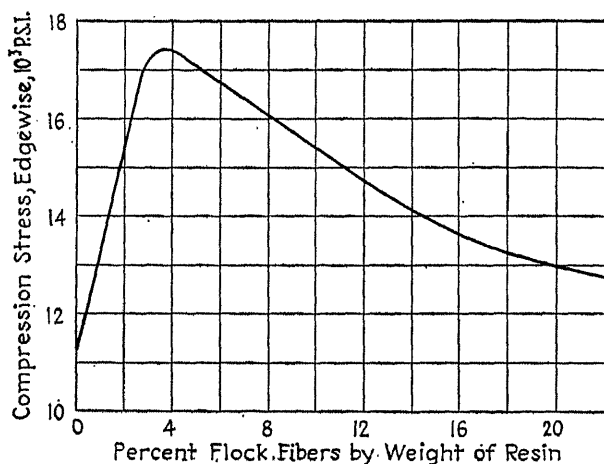


Figure 12. Characteristics of low pressure glass cloth laminate with flock fibers added to bonding resin.

12, reproduced from Major Kemmer's paper, shows the relationship between edgewise compressive strength and the per cent glass flock fibers by weight of the bonding resin. The explanation is probably mechanical rather than chemical, in the relief of stress concentrations characteristic of a more brittle, rigid type of adhesive agent.

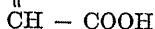
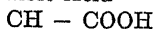
Unsaturated polyester resins have been prepared from a vast number of chemical compounds, and the possibilities are unlimited. The resins are reaction products of unsaturated polybasic acids or unsaturated mono- or polyhydric alcohols, their chlorinated derivatives, their esters, dibasic acid chlorides, or anhydrides. This opens the way to many potential resin-forming reactions. As distinguished from the alkyds, the unsaturated polyesters contain a number of unsaturated ethylenic groups which form cross-linked three-dimensional structures. Vinyl type polymers may be included for copolymerizing with the unsaturated groups in the polyester.

In reviewing the principles of the formation of polyester resins from

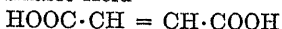
either unsaturated alcohols or esters, the following reagents may be considered:

*Unsaturated Polycarboxylic Acids*

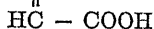
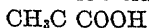
Maleic Acid



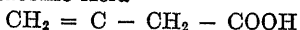
Fumaric Acid



Citraconic Acid



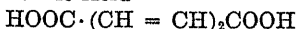
Itaconic Acid



Glutaconic Acid

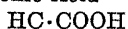


Muconic Acid

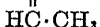
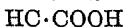


*Unsaturated Monocarboxylic Acids*

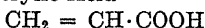
Crotonic Acid



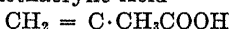
Isocrotonic Acid



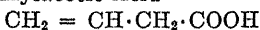
Acrylic Acid



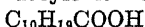
Methacrylic Acid



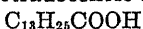
Vinylacetic Acid



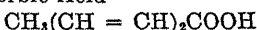
Undecylenic Acid



Tetradecenoic Acid



Sorbic Acid



Cinnamic Acid



*Saturated Polycarboxylic Acids*

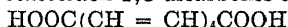
Diglycollic Acid  $(\text{HOOC} - \text{CH}_2)_2\text{O}$

Oxalic Acid  $\text{HOOC} - \text{COOH}$

Hexatrien 1,6 dicarbonic acid



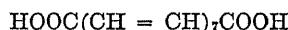
Octatetraen-1,8 dicarbonic acid



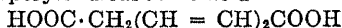
Decapentaen-1,10 dicarbonic acid



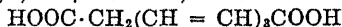
Tetradecaheptaen-1,14 dicarbonic acid



Piperylendicarbonic acid



1,3,5 heptatrien-1,7 dicarbonic acid



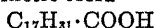
Palmitoleic acid



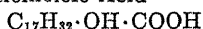
Oleic Acid



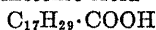
Linolic Acid



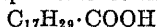
Ricinoleic Acid



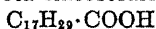
Linolenic Acid



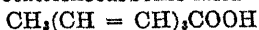
Alpha-elaostearic Acid



Beta-elaostearic Acid



Octatrienecarbonic Acid



Malonic Acid	$\text{HOOC} - \text{CH}_2 - \text{COOH}$
Succinic Acid	$\text{HOOC} - (\text{CH}_2)_2\text{COOH}$
Glutaric Acid	$\text{HOOC} - (\text{CH}_2)_3\text{COOH}$
Adipic Acid	$\text{HOOC} - (\text{CH}_2)_4\text{COOH}$
Pimelic Acid	$\text{HOOC} - (\text{CH}_2)_5\text{COOH}$
Sebacic Acid	$\text{HOOC} - (\text{CH}_2)_8\text{COOH}$

#### Aromatic Polycarboxylic Acids

Phthalic Acid	$o - \text{C}_6\text{H}_4(\text{COOH})_2$
Isophthalic Acid	$m - \text{C}_6\text{H}_4(\text{COOH})_2$
Mellitic Acid	$\text{C}_6(\text{COOH})_6$

#### Unsaturated Alcohols

Allyl Alcohol	$\text{CH}_2 = \text{CH} \cdot \text{CH}_2\text{OH}$
---------------	--

Cinnamic Alcohol  
 $\text{HC} = \text{CH} \cdot \text{CH}_2\text{OH}$

Methallyl Alcohol	$\text{CH}_2 = \overset{\text{CH}_3}{\text{C}} \cdot \text{CH}_2\text{OH}$
Propargyl Alcohol	$\text{CH} \equiv \text{C} \cdot \text{CH}_2\text{OH}$
Crotonyl Alcohol	$\text{CH}_3 \cdot \text{CH} = \text{CH} \cdot \text{CH}_2\text{OH}$
Halogen substituted alcohols of the above	



#### Hydroxy-Substituted Acids

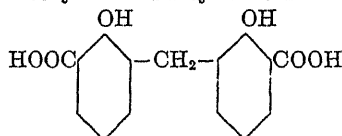
Lactic Acid	$\text{CH}_3\text{CH} - \text{COOH}$ $\begin{array}{c} \text{O} \\   \\ \text{H} \end{array}$
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Glycolic Acid  $\text{HO} \cdot \text{CH}_2\text{COOH}$

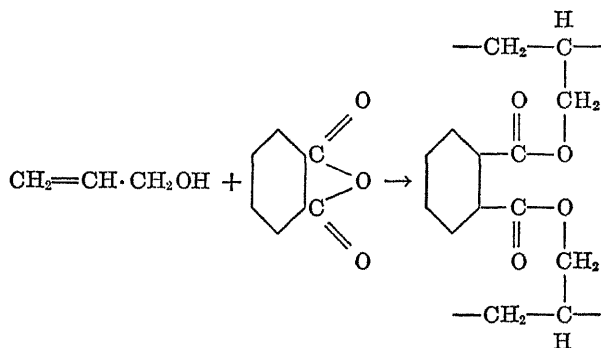
Citric Acid	$\begin{array}{c} \text{COOH} \\   \\ \text{CH}_2 \\   \\ \text{HOCCOOH} \\   \\ \text{CH}_2 \\   \\ \text{COOH} \end{array}$
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Tartaric Acid	$\begin{array}{c} \text{COOH} \\   \\ \text{HCOH} \\   \\ \text{HCOH} \\   \\ \text{COOH} \end{array}$
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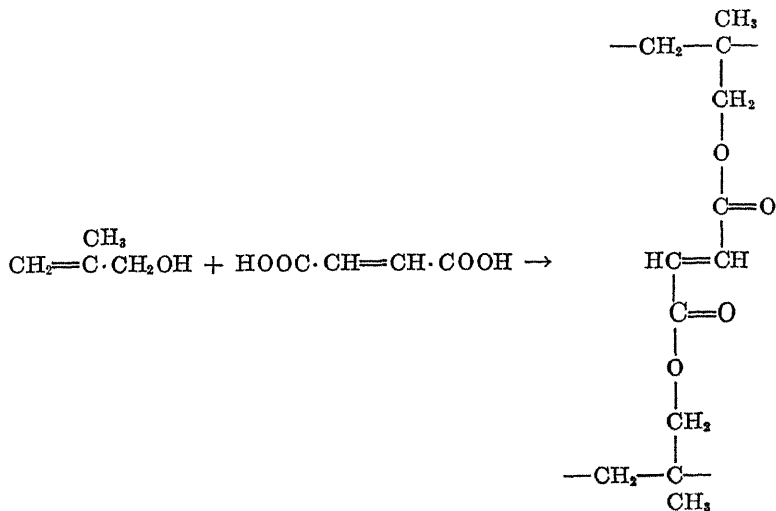
Methylene Disalicylic Acid



From various combinations of the unsaturated alcohols listed above and various ether alcohols such as diethylene glycol,  $\text{O}(\text{CH}_2\text{CH}_2\text{OH})_2$ , or 1,2-propylene glycol, with various unsaturated or polycarboxylic acids, the polyester resins may be formed. Generally they may be activated by benzoyl peroxide, acetyl peroxide, 90% hydrogen peroxide or lauroyl peroxide, or special free radical types of catalysts. From these polyester resins will be found many materials of potential interest to the adhesive field. To illustrate a few of the typical reactions, the following may be considered.

(1) *Unsaturated Monohydric Alcohol plus Dibasic Acid.**Allyl Alcohol Phthalic Anhydride*

Pollack and Chenicek described polymerizable unsaturated alcohol esters of polycarboxylic acid, for example<sup>38</sup>. D'Alerio prepared various resins by polymerizing phthalic di-esters of halogeno-allyl alcohols<sup>39</sup>. Bradley polymerized diallyl fumarate, sebacate, succinate, adipate or phthalate<sup>40</sup>.

*Methallyl Alcohol**Fumaric Acid**Dimethallyl Fumarate*

Rothrock, for example, formed thermosetting resins by polymerizing propargyl fumarate and dimethallyl fumarate<sup>41</sup>. Difumaric esters have been specifically recommended for adhesives and impregnants<sup>42</sup>.

(2) *Esters of Unsaturated Monohydric Alcohol.* Even the esters of allyl alcohol, such as allyl acetate, are capable of polymerizing in the presence of a large amount of benzoyl peroxide. The rate of polymerization

in this instance is not strongly affected by oxygen unless the mixture is stirred vigorously<sup>43</sup>. Esters of alpha-chloroacrylic acid plus acrylic or methacrylic acid are described by Pollack<sup>44</sup>. Copolymers of allyl chloride and vinyl chloride have been prepared<sup>45</sup>.

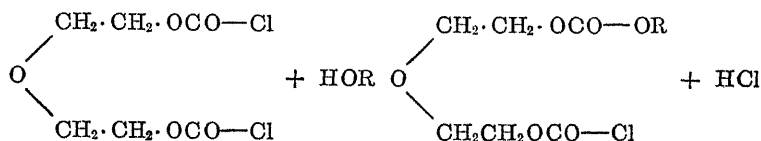
(3) *Unsaturated Polybasic Acids plus Polyhydric Alcohols*. Hard, stable, oil-soluble esters of pentaerythritol and rosin plus unsaturated polybasic acids have formed useful polyesters<sup>46</sup>. Various "adducts" may be used in lieu of polybasic acids, as they will provide carboxyl groups for further reaction. Catlow prepared a resin from 9 to 23 parts of cyclopentadiene "adduct" of maleic anhydride with 100 parts of natural resin and polyhydric alcohol<sup>47</sup>. Itaconic esters (0.1 to 10 per cent) have been specified as cross-linking agents for vinyl chloride by D'Alelio<sup>48</sup>. Polyester resins have been prepared by Bradley from dipentaerythritol, polycarboxylic acids, and unsaturated oil fatty acids<sup>49</sup>. Diethylene glycol ethyl ether esters of polycarboxylic acids were prepared by Bradley<sup>50</sup>. Agens prepared polyester resins from polyhydric alcohols, tetrafurfuryl alcohol, and an unsaturated polybasic acid<sup>51</sup>. Compositions were also prepared of partially polymerized diallyl esters of dicarboxylic acid and an allyl ester by D'Alelio<sup>52</sup>. In a review of industrial applications of fumaric acid, the polymerization of diethyl fumarate, diallyl fumarate, diethylene glycol fumarate was discussed<sup>53</sup>. The latter formed tough, hard resins. Peroxide catalysts were specified.

(4) *Unsaturated Monocarboxylic Acid Esters*. Muskat and Pollack described two-stage polymerization of esters derived from polyhydric alcohols and at least two molecules of unsaturated monocarboxylic acids<sup>54</sup>. D'Alelio formed interpolymers of diallyl itaconate with ethyl methacrylate<sup>54</sup>. Hill, on the other hand, prepared copolymers from methyl methacrylate and polymerizable unsaturated esters<sup>55</sup>. Britton, Coleman, and Zemba prepared polyester resins from unsaturated esters of carboxylic acids over 10 carbon atoms. The acids were esterified with allyl, 2-chloroallyl, and 2-methyl allyl alcohols<sup>57</sup>. Various artificial glasses were prepared from polymerized unsaturated monohydric alcohol and monocarboxylic acids<sup>58</sup>. In polymerizing polyhydric alcohol polyesters of methacrylic acid, the procedure is introduced of separating residual monomer<sup>59</sup>.

Staudinger polymerized styrene in the presence of crotonic acid esters to form a resin<sup>60</sup>. Chlorinated acrylic acid esters were copolymerized with vinyl resins by Arnold, McLeish, and Crawford<sup>61</sup>.

(5) *Saturated Acid Esters*. Examples of unsaturated alcohol mono- and polybasic saturated acids have already been given. Dean prepared polymers from saturated aliphatic monocarboxylic acid esters of allyl alcohol<sup>62</sup>. He described adhesive applications of an interpolymer of polycrotyl ester of a saturated polycarboxylic acid and a polyhydric alcohol ester of maleic,

itaconic, or fumaric acid<sup>63</sup>. Muskat and Strain prepared polydiesters of carbonic acid and lactic acid esters of unsaturated alcohol<sup>64</sup>. Polyester resins are prepared from oxalic acid and unsaturated alcohols. Molding, impregnating, and laminating applications are enumerated. Dimethallyl and diallyl oxalate resins are mentioned in particular<sup>65</sup>.



*Diethyleneglycol bis (chloroformate)*

The above reaction has served as the basis of a number of polyester resins. Availability of the acid chloride at 35 cents per pound has made this material useful to the synthesis of various polymers<sup>66</sup>. A typical commercial resin is diallylethylene glycoldicarbonate used in transparent sheets.

(6) *Butadiene Monoxide* ( $\text{CH}_2 = \text{CH} - \text{CH} - \text{CH}_2$ ). The alpha epoxide



groups of butadiene monoxide and its possible additive reactions with alcohols and acids makes this an extremely interesting raw material from the standpoint of synthesis of polyester resins. Reactions with dibasic acids proceed quite vigorously.

(7) *Copolymers with Vinyl Resins*. Divinyl benzene has been utilized with polyesters to form useful copolymers. D'Alerio combined it with soluble, fusible unsaturated alkyds<sup>67</sup>. He specifically noted allyl, methallyl, and chloroallyl esters of unsaturated acids<sup>68</sup>. Vinyl benzene and vinyl acetate are most frequently used as copolymers with polyesters to toughen them. Cured with heat alone they tend to gel very rapidly but not always to a clear, crack-free structure. The addition of a thermoplastic monomer or partial polymer improves physical properties. Pollack described the use of vinyl and acrylic copolymers with polyesters, specifying the materials for impregnation of wood, leather, and paper products<sup>69</sup>. The advantages have been cited by others<sup>70</sup>. Moffett and Smith copolymerized vinyl chloride and allyl chloride<sup>71</sup>, while vinylidene chloride is copolymerized with various allyl esters<sup>72</sup>. Emphasis is placed upon vinyl acetate in combination with diallyl phthalate and other diesters<sup>73</sup>. Further reactions with aldehydes are cited.

## Miscellaneous Applications of Alkyd Resins as Adhesives

Lawson described a number of useful adhesive products prepared from polycarboxylic acids, such as phthalic acid and succinic acid reacted with

ether alcohols (alkyl or aryl derivatives of glycerol or pentaerythritol)<sup>74</sup>. Adams made general claims for a cementing compound prepared from glyceryl phthalate and a semi-drying oil<sup>75</sup>.

Maleic anhydride and polyhydric alcohol resins in combination with cellulose derivatives were employed as adhesives<sup>76</sup>. Dougan prepared laminations of glass, wood, textiles or cellulose acetate sheets by effecting assembly in a bath of glyceryl phthalate at a low stage of condensation<sup>77</sup>. Mixed alkyd resins were proposed as adhesives<sup>78</sup>. Zola was among the first to recognize the value of alkyd resin adhesives for safety glass, because of their transparency and resistance to yellowing or discoloration. He employed a condensation product of glycerol and sebacic or adipic acid<sup>79</sup>.

Hovey specifies 11 to 20 parts of glyceryl phthalate and castor oil for each 22 to 26 parts of a low-viscosity nitrocellulose in solution of ethyl acetate and toluene, for cementing purposes<sup>80</sup>, though drying oils are also indicated in other formulations<sup>81</sup>. Alkyds were employed in formulating adhesives for cellophane sheets<sup>82</sup>. General improvements in the alkyd resin adhesives were noted by using the resinous products of glycerol, phthalic anhydride, and a monohydric alcohol with at least ten carbon atoms (lauryl, cetyl, oleyl); these were used also to impregnate wood, cloth and paper<sup>83</sup>. In another modification, drying oils were first heated and then condensation products of alkyd resins added to form the adhesive<sup>84</sup>. An adhesive employed for bonding mica flakes or safety glass interlayers was prepared by forming an alkyd with an excess of polybasic acid. Dissolve in water in presence of ammonia, add casein and harden with formaldehyde. A resin of a high acid number is sought for the adhesive<sup>85</sup>. Alkyd resins, with or without fatty acids from drying oils, secured graphite or talc to metallic surfaces to aid self-lubrication<sup>86</sup>. The sulphonamide-formaldehyde resins are employed with the alkyds and cellulose nitrate to form an adhesive lending itself to heat-sealing operations<sup>87</sup>.

Moss developed alkyd resins from citric acid and glycerol, with an optional selection of paraformaldehyde. The water-soluble condensation products formed were applied as adhesives in the manufacture of safety glass employing an interlayer of cellulose acetate. Good compatibility with the cellulose ester was evident<sup>88</sup>. In addition to the bonding of safety glass, which is the most frequently mentioned application of a kyd resins, their application to metal surfaces is important. Good specific adhesion of alkyd resins upon metal surfaces is well known, as evidenced by the many metal surfaces protected by these resins. However, very little attempt has been evident in the use of alkyds as a cementing aid. Ensminger suggested a technique which fundamentally shows much prom-

ise in bonding metals to other materials<sup>89</sup>. The metal is coated with a primer of alkyd resin. This is followed with an adhesive which bonds to the alkyd and other surface.

Frequent mention is made of the use of alkyd resins in the manufacture of sandpaper and other abrasive particles. Pellet employs drying oil-modified alkyd resins and phenol-formaldehyde condensation products as water-proof binders for abrasive particles<sup>90</sup>. Alkyd resin adhesives in abrasives are described in another reference<sup>91</sup>. Guth prepared a water-proof sandpaper of low gumming qualities with the aid of a glyceryl phthalate compound (15 to 45 per cent) and a flexibilizing and gelatinizing compound (15 to 50 per cent)<sup>92</sup>. Various oils were employed as flexibilizing agents. It is important to hold the abrasive particles tenaciously as well as maintain a high wet strength. Orgy and Foss employed an adhesive mix of an alkyd resin and urea-formaldehyde condensation product to join the ends of an abrasive belt into a continuous link<sup>93</sup>. Alkyd resins for the abrasive industry have been reviewed<sup>93a</sup>.

Roller developed a fire-resistant adhesive for wood or glass, embodying an alkyd resin as the major component, and flame-resistant plasticizer, drying oils, and a small amount of rubber in solution<sup>94</sup>. Among the plasticizers mentioned were beta-naphthol; dibutyl phthalate; tricresyl phosphate; and triphenyl phosphate. An adhesive for bonding aluminum to cork compositions comprises glyceryl phthalate, castor oil, cellulose nitrate, and 1 to 10 per cent of wax<sup>95</sup>. Good adhesive properties are noted in coatings of reaction products of castor oil and halogenated fumaric acid or other polycarboxylic acids<sup>96</sup>. In another metal coating and adhesive product, alkyd resins are applied to metal foils designed for perishable foods<sup>97</sup>. Rothrock also prepares a thermoplastic composition for hot melting, and then coating foils comprising a glycerol-maleic-rosin product, ethyl or benzyl cellulose, and 0.2 to 1 per cent of triphenyl phosphate<sup>98</sup>.

A form of alkyd resin was prepared by Lasher for cracks or seams in gasoline tanks by heating blown castor oil (20 parts) with 11 parts of citric acid at 400°F for several minutes. Asbestos fiber and zinc chromate are added to the resin to improve the adhesion to metal surfaces<sup>99</sup>. Special problems are sometimes required of the transparent alkyd resin adhesive. Optical elements with a refractive index of 1.45 to 1.8 and bonded with a synthetic resin of refractive index 1.5 to 1.6 comprise one typical assembly<sup>100</sup>. In these and other ways, the alkyds are finding new and significant applications in the adhesive field. Polyester resins have also been used as replacements for Canadian balsam in cementing optical goods<sup>101</sup>. Permanently tacky adhesives for tapes have been developed from maleic anhydride and castor oil, plus vinyl acetate<sup>101a</sup>.

### Resins from Furan Derivatives

A newcomer to the field of plastics and their resin adhesives—the furan group—shows much promise of being able to compete successfully with other thermosetting-resin adhesives. Furfural, obtained commercially from vegetable by-products such as corncobs and oat hulls, serves as the starting point in the synthesis of a number of useful derivatives based on the furan ring. Furfuraldehyde (furfural) and furfuryl alcohol are the two best known members of this series; both are capable of undergoing resinification in the presence of acidic catalysts. Thermosetting adhesives prepared from these compounds are unique, largely because of the excellent solvent characteristics of the furan compounds in their unpolymerized state. Most of the synthetic resins, such as polyvinyl acetate, polyvinyl butyral, polymethyl methacrylate, polyvinyl chloride, polyvinyl alcohol, phenol-formaldehyde, glyceryl phthalates, and urea-formaldehyde, can be dissolved by furfural or furfuryl alcohol. Similarly, cellulose ethers and esters are soluble in these materials. This was observed by Gardner shortly after the furan solvents became commercially available<sup>102</sup>, while Ellis polymerized furfural with acids<sup>103</sup> in the presence of nitrocellulose. Similarly, Payne and Seymour prepared an acid-resisting cement by dissolving polyvinyl butyral in furfuryl alcohol, and polymerizing the combination with an organic acid catalyst, having an ionization catalyst (based on water) not less than  $0.38 \times 10^{-4}$  at 25°<sup>104</sup>. Adherent metal coatings were indicated by Kauth, who combined furfuryl alcohol and alkyd resins<sup>105</sup>, while Lewis produced combinations of furan derivatives with the copolymer of polyvinyl chloride-acetate<sup>106</sup>. These are a few of the numerous combinations of the furan derivatives with high polymers, and tend to bear out the good compatibility of the materials. Furfural may even serve as a solvent for various inorganic salts, as the quantitative examinations of Trimble brought out<sup>107</sup>.

The mechanism of the polymerization of furfural and furfuryl alcohol has not been the subject of detailed published investigations, though Dunlop and Peters observed an intermolecular dehydration during storage<sup>108</sup>. Ever since Trickey's pioneer work on the resinification of these derivatives with acid catalysts<sup>109</sup>, it has been a recognized fact that polymers may be formed from furfural, furfuryl alcohol and their combination, in the presence of acid catalysts; addition products in the presence of strongly alkaline catalysts; and the Cannizzaro reaction in the effect of mild alkalis on furfuraldehyde.

Furfuryl alcohol will resinify much more rapidly than furfural; comparisons may be drawn by resinifying furfural and furfuryl alcohol in contact with different percentages of acidic catalyst and observing the gelling time of small quantities at 100°<sup>110</sup>. Figure 13 brings out the differ-

ence between the rates of polymerization of the two materials at 100°. Furfural in the presence of strong acid catalysts will resinify to a black, friable solid which will check and crack readily. Gel formation is rapid,

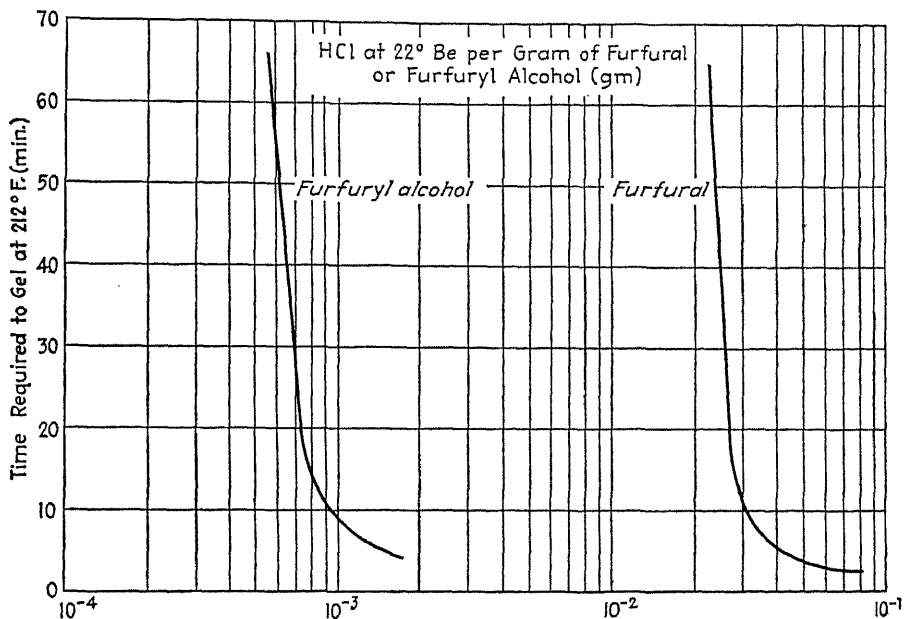
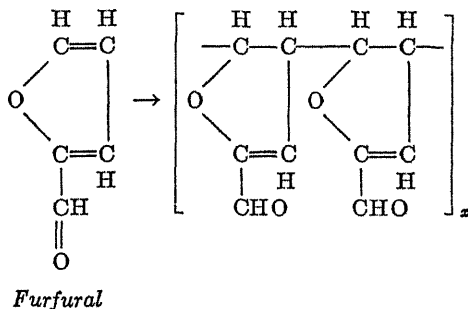


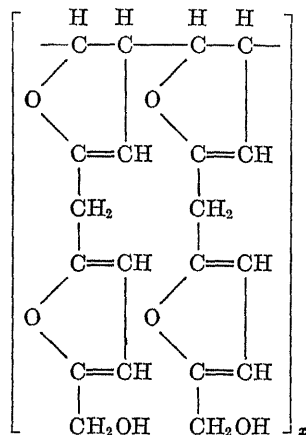
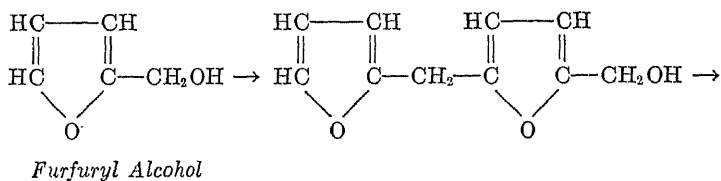
Figure 13. Resinification rates of furane derivatives

and it is likely that low molecular weight polymers are formed. The mechanism of the polymerization is as follows:



On the other hand, the resinification of furfuryl alcohol is accompanied by the formation of water, though it has been the writer's experience that the rate of water formation is not appreciable until just before gelling, when there is a marked rise in viscosity of the polymer, a sharp decrease in the available OH groups on the furfuryl alcohol polymer, and a visible

separation of water. Small addition agents have marked effects on the character of the polymer formed, though polymerization may be presumed to follow the pattern indicated below. The water formed early in the reaction is probably retained by the unpolymerized fractions (which, unlike furfural, are water-soluble), until they too, are polymerized, the water inhibiting the rate of resinification of the unpolymerized portions.



The structure of the furfuryl alcohol polymer should admit the presence of free hydroxyl groups capable of cross-linking and forming water at the time of the final gelling. Furfuryl alcohol polymers are also interesting in that during resinification after the addition of an acidic catalyst, there is an immediate increase in hydrogen ion concentration, followed shortly thereafter by a slow decrease in H-ion concentration (rise in pH). The furfuryl alcohol liquid polymers also lend weight to the sphero-colloid theory of thermosetting polymers. After a resin of approximately 150 to 200 centipoises viscosity has been formed, the polymer is distinguished by the appearance of small globules or concentrations of various sizes, which can be readily studied when spread on a glass plate. As the resinification proceeds to a very viscous state and to the final infusible, insoluble state, the globules tend to fuse into a homogeneous mass.

Liquid polymers prepared from furan derivatives may be made stable indefinitely, which is a decided advantage, considering the poor storage characteristics of the cold-setting liquid urea or phenol-formaldehyde

resins. When activated with small amounts of acid catalysts, they may be made to cure at room temperatures. The resin adhesive is decidedly hydrophobic in character, and develops a waterproof bonding which will not break down under long immersions in cold or boiling water. They are particularly effective in the bonding of thermosetting laminated phenolics<sup>111</sup> developing shear strengths at the glue line up to 4500 p.s.i. for  $\frac{1}{4}$  inch stock, which results in delamination of the laminated canvas or paper at the time of failure (see Figure 14). Other thermoplastic polymers and rubbers are very effectively bonded with furan resin adhesives. Due to the hydrophobic nature of the resin, best results are obtained when the

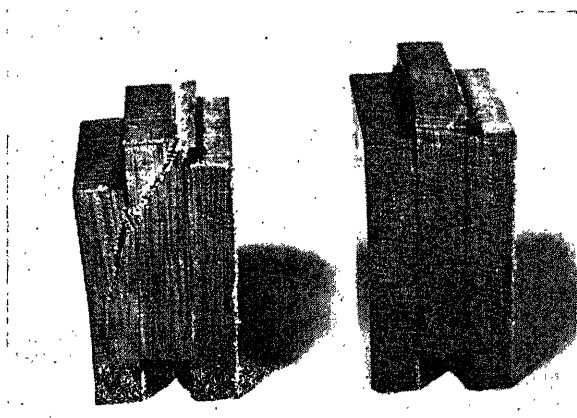


Figure 14. Laminated phenolic bonded with furane adhesive (failure at 4500 psi.)

surfaces to be bonded are dry, and in the case of laminated phenolics, in an *unsanded* condition. Considerably better results are obtained upon a smooth surface, indicating a very high specific adhesion for the phenolic surfaces. Bond strengths are obtained on laminated phenolics in excess of the shear strength of the laminate.

Furan resin adhesives have afforded an excellent opportunity of comparing the relative merits of a substantially 100 per cent liquid thermosetting adhesive with one containing some volatiles. Much greater strengths are obtained for thick glue lines with this high solids adhesive than is possible for the conventional adhesive with volatiles. The technique has been likened by the writer to a casting-gluing process. Shear strength versus glue line thickness shows no loss in strength up to 0.032". As a matter of fact, slabs of the furan adhesive may be cast and physical properties readily evaluated, which is not readily possible with adhesives containing volatile constituents.

To permit a comparison with the resorcinol and urea adhesives already

illustrated, the furan resin adhesives (Resin X-2) are analyzed in Figures 15 and 16 after different pot lives and open assembly times of 0 and 20 minutes. Tests were performed on unsanded laminated phenolic canvas, at room temperature upon fully cured glue lines. Long pot life features the more recent furan resin adhesives (Resin X-2). This is one of the most important practical aspects of any low temperature-setting glue.

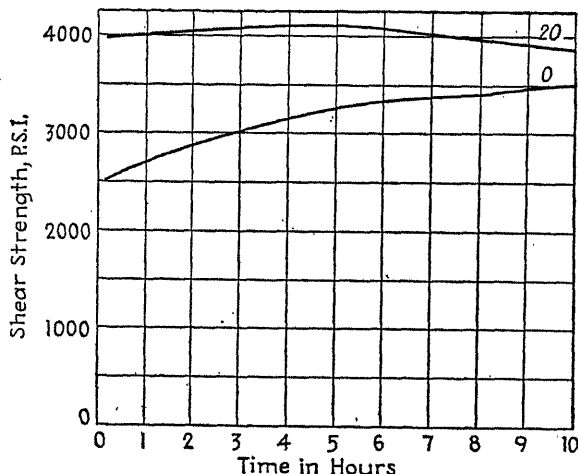


Figure 15. Characteristics of furane resin adhesive on phenolic canvas laminates. Variables shown are time in minutes after adding catalyst before adhesive is applied and two open assembly periods after application of the adhesive. All assemblies were cured one week at room temperature before test.

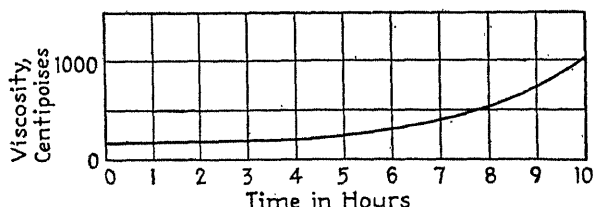


Figure 16. Viscosity characteristics of furane resin adhesive after adding catalyst

The bonding of porous cellulosic products entails special problems for the liquid furan resin adhesives which contain ingredients with good wetting and penetrating properties. These properties may be as serious a factor in causing localized embrittlement as a highly acid glue below a pH of 2.0. Consequently, for bonding porous cellulosic materials the adhesives are prepared or applied so that penetration is reduced. Then the exceptionally high strength of the furan resin adhesives can be realized.

There are cases, however, when it is highly desirable to take advantage of the good penetrating and binding qualities of the furan resins. For example, Delmonte impregnated plaster of paris forms with furan resins

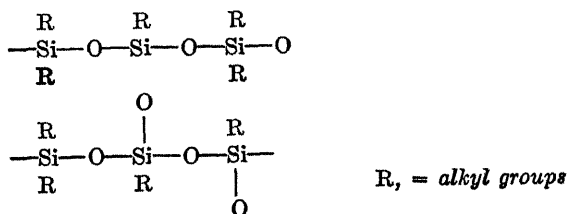
with good results<sup>112, 113</sup>; a three to four-fold improvement was achieved. Even more superior characteristics are noted when various flock fillers are introduced into the plaster structure, the furans welding the assembly into a strong structure.

The combination of phenol-formaldehyde partial polymers and furan resin partial polymers has been suggested as yielding a superior type of resin<sup>111</sup>. Among other applications of note is the manufacture of abrasive sheets by Hadnagy, employing polymerized furfuryl alcohol<sup>114</sup>. Industrially, however, the largest markets developed for furfural have been as a selective solvent to remove unsaturates from the butadiene manufacturing process during the preparation of synthetic rubber, and in processes for purification of rosin.

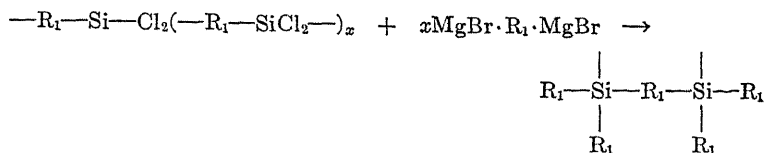
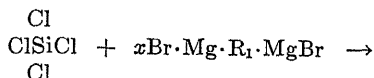
### Silicone Resin Adhesives

Silicone resins were introduced commercially for the first time during 1944, though they have been the subject of much research work during the past ten years or thereabouts. Their initial applications included fluids having little change in viscosity over a wide temperature range, chemically resistant greases and rubber-like products, and electrical insulating varnishes. While at the present time it is much too early to predict the possible adhesive applications of the silicone resins, certain specific claims have been made for their adhesive properties in various patents. In addition, the impregnation and bonding of woven glass laminates have given evidence that the silicones in some forms possess thermosetting properties. By co-condensation of methyl silicols with phenyl silicols, a resin of high initial tack and viscosity was obtained for bonding laminates<sup>115a</sup>. Liquid silicone resins will render clean, grease-free surfaces non-wetting. This fact has been invaluable to the protection of ceramic insulators and in rendering them waterproof.

It is generally recognized that Kipping's early efforts in the field of organo-silicon compounds did much to arouse interest in this field, though until recent years his efforts were not marked by any commercial recognition. However, Kipping first recognized that silicanediols condensed intermolecularly to yield polymeric anhydrides and silicones<sup>115</sup>. Rochow and Gilliam were the first to report on the silicone resins in this country, describing a solid polymer formed by condensing the silicanediols with the silicanetriols<sup>116</sup>:

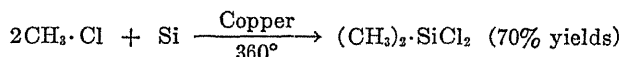






surface, forming the hydrochloric acid, which evaporates, and the silanols which possess such excellent water-repelling qualities<sup>120</sup>. Generally, however, silicones are not compatible with other organic high polymers. The high-temperature resistance of the silicones will undoubtedly make them excellent binders for abrasive grinding wheels, and should be superior to the organic types intended for this purpose. Silicone resin adhesives should be developed with high specific adhesion for ceramic surfaces.

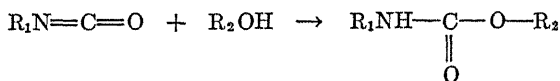
Hyde prepared some silicone resins by heating  $\text{R}\cdot\text{R}^1\cdot\text{SiCl}_2$  at 170 to 180°, followed by the addition of moist air<sup>121</sup> (R is an alkyl group and  $\text{R}^1$ , an aryl group). Elastic, rubber-like silicone resins retaining their flexibility at high temperatures have been announced by General Electric Co.<sup>122</sup> and Dow Corning Corp.<sup>123</sup>. Rochow has described the direct synthesis of organosilicon compounds without the necessity of the Grignard reagent<sup>124</sup>. The reaction was found to be general between hydrocarbon halides and silicon in the presence of copper or copper alloys.



Phenyl chlorosilanes have also been produced directly from chlorobenzene and silicon<sup>129</sup>. Hurd has also observed that finely divided aluminum and zinc may be used to catalyze the reaction of chlorosilanes and alkyl halides at 300 to 500°<sup>125</sup>. Hyde described a method of increasing viscosity of organosilicon compounds by passing oxygen through them at 200 to 300°<sup>127</sup>. Silicone anti-foam agents have been developed for aqueous emulsions<sup>123</sup>. They are effective in low concentrations.

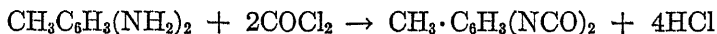
### Polyurethanes

Kline described the polyurethanes in his report on wartime plastics developments in Germany<sup>126</sup>. The isocyanates may be prepared by action of alkyl halides on potassium cyanate or by the oxidation of isonitriles. They are quite reactive and combine with alcohols in the following manner:



*Alkylisocyanate*

For the synthesis of polyurethanes, di and tri-isocyanates are prepared. In Germany, tolylenediamine, prepared by nitration of o-nitrotoluene, followed by reduction, served as the intermediate in the preparation of tolylene di-isocyanate. Reaction was carried out in an o-dichlorobenzene solution of phosgene ( $\text{COCl}_2$ )<sup>130</sup>:



The chief polyhydroxy compounds employed for reaction with the polyisocyanates to form the polyurethanes, were 1,4 butanediol and hexanetriol. A group of resinous adhesives ("Polystal") showing excellent adhesive characteristics for wood products were prepared from combinations of polyurethanes and polyesters (from adipic acid and trimethylolpropane). While thermosetting qualities were displayed, the adhesives were more flexible than phenolics or ureas.

Another polyisocyanate which found important war use as a metal-rubber adhesive, was prepared from triamino-triphenylmethane, through reaction with phosgene. The addition of 2% of this compound to synthetic rubber formulations improved adhesion to tire cords.

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## Chapter 5

### Polyvinyl Resin Adhesives

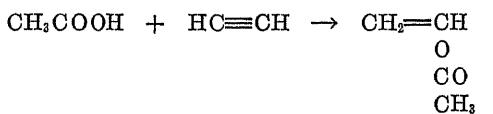
Polyvinyl resins have been long prominent in the field of synthetic resin adhesives. No newcomer to the plastics industry, they have gained wide acceptance in the coating, extruding, and fabricating fields. There have been a large number of noteworthy adhesive developments, not only in the polyvinyl esters, polyvinyl acetate, polyvinyl chloride, polyvinyl dichloride, and their copolymers, but also in polyvinyl alcohols and polyvinyl acetals, including thermosetting modifications of the latter. Polyvinyl ethers are not employed to any large extent in this country, their adhesive properties have nevertheless attracted attention abroad; they will therefore be included in the general examination of polyvinyl resins and their adhesives.

Probably the greatest emphasis has been placed upon the development of adhesives from polyvinyl acetate. These adhesives are sold in a number of forms and solutions, possessing different softening points and different degrees of polymerization. A casual impression of the solids would be that they are readily softened by heat, becoming quite sticky as the temperature is raised, and then if the temperature becomes too high, evolving a strong odor of acetic acid. Other characteristics which are readily recognized include the excellent compatibility of polyvinyl acetate with other synthetic resins and various plasticizers and solvents. In this respect it has a decided advantage over the chlorinated polyvinyl esters, which are not as compatible or as soft. As a general-purpose adhesive for porous and some non-porous materials polyvinyl acetate adhesives have found wide acceptance.

Klatte prepared vinyl acetate for the first time in 1912 by passing acetylene through acetic acid in the presence of a mercuric sulfate catalyst<sup>1</sup>. It is still prepared by this method, though activated charcoal and zinc acetate are now used as catalysts. The importance of peroxide catalysts for the polymerization of vinyl acetate was also recognized at this early date<sup>2</sup>. It is difficult to determine exactly when the polymer attained industrial importance, because while it was introduced in Germany in 1915, apparently very little was done with the material for about fifteen years. Likewise in this country, vinyl acetate was first considered incidental and

as a by-product of the manufacture of ethylidene diacetate, a source of acetic anhydride<sup>3</sup>. Real progress was made in 1929 when the reaction products of certain aldehydes and polyvinyl acetate were patented<sup>4</sup>, forming a number of useful polyvinyl acetals, some of which have excellent adhesive properties.

The general reaction of acetylene upon acetic acid may be illustrated in the following manner, this procedure also serving for the preparation of a number of polyvinyl esters:

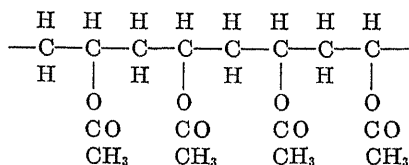


*Vinyl Acetate*

Commercial vinyl acetate monomer has a boiling point of 71.8–73.0°, with a purity of over 99.5 per cent. A copper salt which is generally added to prevent polymerization may be removed by distillation. Iron and sulfur will also retard the polymerization, necessitating porcelain-enamelled, aluminum, or stainless steel polymerization equipment. Various degrees of polymerization can be obtained through choice of catalyst, control of temperature, or the nature of solvent in which vinyl acetate may be polymerized. The degree of polymerization may vary from 30 to 900 units in the chain, though the more common commercial types range from 60 to 230 units. The purity of the monomer has a decided bearing on the final degree of polymerization; for example, small traces of acetaldehyde will influence the results. If the acetaldehyde trace is excessive it will inhibit polymerization; yet others have pointed out that absolutely pure vinyl acetate requires a trace of peroxide to polymerize, suggesting that a small trace of peroxide derived from acetaldehyde ( $\text{CH}_3\cdot\text{CHO}$ ) will catalyze the reaction<sup>5</sup>. It is generally recognized that the stronger the peroxide concentration, the more rapid the rate of polymerization.

Polymerization in solution affords an effective method of controlling the polymerization of vinyl acetate, because it reduces the hazards of the strong exothermic reaction involved and leaves the resin in a solution form, convenient for further blending or modification. The nature of the solvent has a marked effect on the average degree of polymerization attained, benzene permitting a fairly high degree, though toluene exerts a notable retarding action. Low-boiling petroleum ether is a good solvent for the monomer, and polymerization is rapid. The polymer is insoluble and separates out as formed, though as high as 20,000 average molecular weight may be reached. Chlorobenzene, acetone, toluene, and alcohol give low molecular weight polymers.

The "head-to-tail" mechanism is generally accepted as the form of the polyvinyl acetate polymer. Starkweather and Taylor followed the polymerization of vinyl acetate through volumetric contraction and established a linear relationship between the fractional volume contraction and the degree of polymerization by density measurements. They concluded that the polymerization of vinyl acetate is substantially a chain reaction<sup>6</sup>. Recent x-ray diffraction studies show the 1,3 "head-to-tail" polymer of polyvinyl acetate<sup>7</sup>:



*Polyvinyl Acetate*

As adhesives, polyvinyl acetate resins are generally known in solution form, involving a solution of the polymer in methyl acetate (28 per cent solids), toluene (24 per cent solids), and acetone (35 to 70 per cent solids, depending upon whether a high or low molecular weight resin is employed). There is a limited use of the vinyl acetate monomer as a solvent type adhesive in some of the solvent cements for polymethyl methacrylate, with which it is compatible. Industrial uses for the polyvinyl acetate resins are largely as coatings and adhesives, inasmuch as molded parts are generally better served by other materials. Several commercial types of these polymers are employed as adhesives; they are identified by their softening point as determined by a modified ball and ring method, and by their solution viscosity. Typical polymers of one manufacturer are shown in the table below<sup>8</sup>:

Concentration by Weight of Polyvinyl Acetate in Various Solvents at Constant Viscosity of 250 cps. at 20° C.

Solvent	Softening Point→				
	Commercial				
	Designation→				
	44°	66°	77°	86.5°	88.5°
	AYAB	AYAA	AYAF	AYAT	AYAW
Acetone (%)	53	39	31	26	17
Toluene (%)	47	32	26	22	14
Butyl Acetate (%)	45	31	25	21	13

In adhesives, types AYAB and AYAF and a modified polyvinyl acetate adhesive are the most popular. Staudinger's work on viscosities has also been confirmed by finding an approximately linear relationship between molecular weight and the viscosity of polyvinyl acetate in benzene<sup>9</sup>. The application of polyvinyl acetate adhesives from a solution generally involves dipping or brushing, inasmuch as in spraying the resin would tend to string out in the form of fine fibers. On the other hand, lacquer-phase

emulsions of polyvinyl acetate resins may be prepared quite readily. They have the advantage of high solids content, without the stringing out tendencies of solutions of polyvinyl acetate in organic solvents. A typical plasticized polyvinyl acetate resin emulsion may be prepared as follows<sup>3</sup>:

	50.0 polyvinyl acetate
	5.0 plasticizer
82.0% Lacquer Phase	43.5 toluene
	1.5 oleic acid
	92.0 distilled water
18.0% Water Phase	8.0 28% aqua ammonia

The ammonium oleate formed in the above combination makes an effective emulsifying agent, inasmuch as after film formation the ammonia is liberated to form a film more resistant to water. While the general resistance of polyvinyl acetate films to moisture is good, the modified types are swollen quite appreciably.

One of the most important problems in adhesion confronting the polyvinyl acetate resin adhesives and most thermoplastic resin adhesives is the evaporation of solvent from the film or glue line. The presence of solvent or volatiles will not only reduce the strength of the bond, but greatly accelerate creep under stress. Polyvinyl acetate solution adhesives have a high initial tack, which is well suited to the bonding of porous cellulosic materials that must adhere firmly to one another when assembled. On the other hand, polyvinyl acetate has a high affinity for solvents, and solvent retention is quite pronounced. In large assemblies of non-porous materials, such as sheets of organic plastics, glass, or sheets of metal, there is little likelihood that all the solvent will be removed from the glue line, if one wants to take advantage of the initial tack rendered by the solvent-wetted adhesive. Only by forced drying of the open glue line and subsequent application of heat welding may the advantages of the adhesive be fully realized. Another effective method is to employ a polymerizable solvent for the polyvinyl acetate. Force-drying of most polyvinyl acetate films can be accomplished at 100 to 150°.

The diffusion of solvents through paper or leather stocks may be quite rapid and solvent removal is not too acute a problem for the non-porous surfaces, permitting early disappearance of volatiles. The effect of solvent evaporation may be ascertained by examination of the shear strength of polyvinyl acetate upon the assembly of non-porous materials such as steel blocks, for different open assembly times at 25°. The author performed a group of tests, shown in Figure 17, which demonstrates that immediate assembly after application of the polyvinyl acetate adhesive results in very low strength, while highest strength is realized after at

least partial evaporation of the solvent. As the film loses its tackiness the strength falls off again. When these values are compared with the results of heat sealing of the same blocks upon complete evaporation of solvent from the adhesive, they are relatively low. All tests were performed with a film of initial thickness of three mils applied from a 30 per cent solution of VYAF polyvinyl acetate in acetone. For comparison purposes, the loss of volatiles was also determined at the same time by evaporation from the surface of thin non-porous phenolic sheet, the weight of which was comparable to the glue line weight, in order to increase the sensitivity of the readings. All test specimens noted above were conditioned for 24 hours at 50° under a light clamp pressure of 20 to 25 pounds

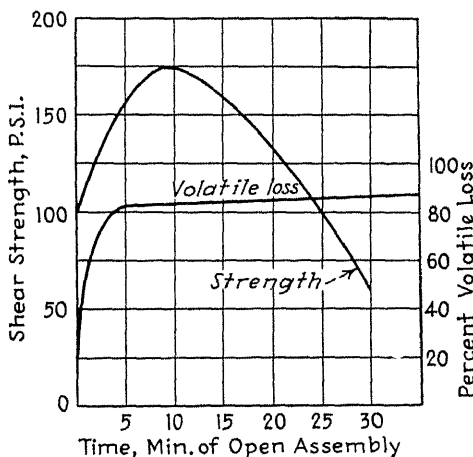
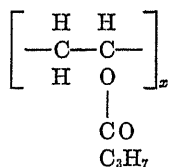


Figure 17. Polyvinyl acetate adhesive applied from solvent. Shear strength of assembly developed at room temperature.

per square inch; total glue line area for each specimen was two square inches.

As to why polyvinyl acetate exhibits good general adhesive properties, one may find some explanation in the acetate radicals attached to the main  $-C-C-C-$  chain. The polar carbonyl group is attached to the polymeric chain by a rotatable oxygen linkage, permitting favorable polar adjustments to the surfaces being bonded, which are so important to obtaining good specific adhesion. On this basis, one would expect other polyvinyl esters to exhibit good adhesive properties, and such is the case, though not in the volume enjoyed by polyvinyl acetate. For example, polyvinyl butyrate (see below) has enjoyed adhesive applications<sup>10, 11</sup>, as has polyvinyl chloroacetate also. In some instances, a mixture of two polyvinyl esters, the acetate and butyrate, offer good adhesive properties, particularly with different degrees of polymerization<sup>12</sup>.

*Polyvinyl Butyrate*

Strother and Patton report considerable improvement of the adhesive strength of polyvinyl acetate for non-porous surfaces by replacing 14 to 35 per cent of the ester groups in the polyvinyl ester with hydroxyl groups<sup>13</sup>. The solubility characteristics are considerably decreased when more than 51 per cent of the ester groups in the macromolecule is replaced. In preparing the above material, polyvinyl acetate is dissolved in 1,4-dioxane and reacted under anhydrous conditions with a lower aliphatic alcohol in the presence of hydrochloric acid. The latter is neutralized at the end of the reaction. In applications of this modified polyvinyl acetate adhesive, the bonding of metal products is cited. Good impact qualities are also claimed.

The good general adhesive properties of polyvinyl acetate were recognized from the earliest days, when it began to attain industrial recognition. Applied to papers and fabrics in combination with various solvents and fillers, polyvinyl acetate made possible various assemblies, generally with the aid of heat and pressure<sup>14</sup>. Heat of course would be required if the solvent evaporated during the assembly period. Recognition of its cementing as well as impregnating qualities was also forthcoming<sup>15</sup>. The addition of plasticizers, particularly isobutyl phthalate dissolved in methyl alcohol, was employed in various adhesive formulations<sup>16</sup>.

Walsh and Caprio interposed partially polymerized polyvinyl acetate between the materials to be assembled, such as woods, metal, and stone, added catalyst and continued the polymerization *in situ* to effect the bond<sup>17</sup>. Polyvinyl acetate has also been recommended for the bonding of abrasive materials to steel discs<sup>18</sup>, and for uniting thin layers of cellulose derivatives<sup>19</sup>. In the latter applications cellulose derivatives were employed in combination with polyvinyl acetate as the adhesive. Dissolved in ethyl acetate, it was generally used as an adhesive for metals, cellulosic films, and glass sheets<sup>20</sup>. Specific advantages were observed by combining the polyvinyl acetate resins with cellulose esters or cellulose ethers in the manufacture of various adhesives<sup>21</sup>. Polymerized and oxidized animal and vegetable oils, as well as polymerized polystyrene and acrylic resins; were also combined with the vinyl esters. In this example, the vinyl acetate was polymerized in the presence of the other polymers<sup>22</sup>. Specific claims of improved performance have been made by Herrmann and Hoehnel

toward adhesive products from polymerized vinyl compounds and cellulose derivatives<sup>23</sup>.

Polyvinyl acetate and plasticizer as an adhesive for photographic film make a good combination<sup>24</sup>. The idea has been extended to the manufacture of laminated identification cards and printed matter, by applying polyvinyl acetate adhesive to the surface to a transparent sheet of cellulose acetate. By inserting the photograph of printed material between sheets of cellulose acetate so treated, applying pressure and some heat, permanent assembly is effected<sup>25</sup>. Adhesive layers of polyvinyl acetate are suited not only to the bonding of cellulose derivatives, but have also been employed to unite cellulose ester films to films of chlorinated rubber<sup>26</sup>. It may sometimes prove advantageous to protect the layer of polyvinyl acetate on the sheet of cellulose derivative by a thin film of cellulose nitrate, which at the time of assembly disappears into the polyvinyl acetate layer under heat and pressure<sup>27</sup>.

Colorless, transparent, and resilient, the adhering layers of polyvinyl acetate provide a good bond for cellulose esters to plate glass in the manufacture of automobile safety glass<sup>28, 29, 30</sup>. A solution of polyvinyl acetate in alcohol or in ethyl acetate may be employed for cementing a layer of cellulose derivative between two sheets of plate glass.

In adaptation to various tapes and labels, polyvinyl acetate has generally been activated with the aid of a solvent, which will remoisten the adhesive layer to render it tacky. Kallander and Alden apply this principle in developing an adhesive tape<sup>31</sup>. They have also prepared a liquid adhesive comprised of 40 parts of polyvinyl acetate, 4 to 12 parts of cellulose ester and 60 parts of a mutual, though volatile solvent<sup>32</sup>.

There has been some use of polyvinyl acetate as coatings and adhesives in the inside of metal cans. A composition prepared of 200 grams of 35 per cent polyvinyl acetate in toluene and 100 grams of a 65 per cent solution of glyceryl phthalate, 75 grams of acetone, and 4 grams of liquid petrolatum has been used<sup>33</sup>. In another example of the combination of polyvinyl acetate with an alkyd, the condensation product of maleic anhydride and 1,3-butylene glycol was found to increase the adhesion of polyvinyl acetate to glass<sup>34</sup>. The copolymer of vinyl acetate and acrylate may be substituted for the polyvinyl acetate adhesive<sup>35</sup>.

Hyde proposed the use of polyvinyl acetate adhesive for cementing together glass blocks or bricks<sup>36</sup>, while McGregor and Warrick improved the bond by employing a hydrolyzed silicate ester plasticized with polyvinyl acetate or polyvinyl *acetal* resin<sup>37</sup>. Improvement of the adhesiveness of polyvinyl esters by silicic esters was noted earlier. In this instance, 3 per cent ethyl silicate was incorporated into a polyvinyl acetate adhesive for safety glass manufacture<sup>38</sup>. Polyvinyl acetate has also been men-

tioned as an adhesive material for siliceous fibers. The fibers are coated with the polyvinyl acetate in solution, and then raised to high temperatures to increase the adhesiveness and promote the bond<sup>39</sup>.

In a further development of adhesive tapes with polyvinyl acetate, Kallander prepared the following composition: Polyvinyl acetate softening at 70°, 60 parts; a fluxing resin comprised of rosin-modified alkyd, 20 parts; shellac, 20 parts. This composition proved useful on paper tapes<sup>40</sup>.

Robinson has recognized the value of polyvinyl acetate adhesives in hot melts without resorting to the use of solvents, the retention of which by the adhesive layer or paper may endanger foodstuffs, as in the manufacture of fibrous containers. From 60 to 75 parts of polyvinyl acetate and 25 to 40 parts of dammar gum are melted together and applied at 150 to 230° to the fibrous material comprising the container, for sealing and making tight seams and joints. This adhesive will not open up in subsequent dips of the container in hot paraffin wax<sup>41</sup>. In another example, pentaerythrityl abietate resin replaced the dammar gum in the same application as noted above. Polyvinyl acetate (70 per cent) was blended with pentaerythrityl abietate ("Pentalyn") at elevated temperatures without the benefit of a solvent<sup>42</sup>. Another thermoplastic sealing adhesive for fiber container joints comprises 60 per cent polyvinyl acetate and 40 per cent pinewood pitch with low solubility in petroleum hydrocarbons<sup>43</sup>.

Polyvinyl acetate has also been employed as a binder for wood flour in the manufacture of the so-called "plastic wood", which is useful as a general patching medium, hardening upon the evaporation of solvent, such as acetone<sup>44</sup>. Halls devoted considerable attention to the evaluation of the polyvinyl acetate adhesives in comparison with other synthetic resins. He described a metal-glass bond from which on a straight pull conchoidal pieces were pulled directly out of the glass<sup>45</sup>. Most of the tests were performed by overlapping dissimilar materials and evaluating the qualities of the bond as excellent, good, poor, and very poor. Two polyvinyl acetates were included in the comparison, one with a rated acid value (milligrams of KOH per gram of resinous base) of 15.5 and the other with an acid value of 1.3. The former was considerably superior, giving excellent results in bonding plywood to plywood and good results upon laminated phenolics. Poor results were encountered in rubber and brass bonds. The development of excess acidity in polyvinyl acetate and other esters, such as the propionate, benzoate, and formate is generally inhibited by 0.01 to 0.1 per cent of diphenylamine<sup>46</sup>.

While solutions of polyvinyl acetate have attracted most interest as adhesives, one should not overlook the possibilities of polyvinyl acetate emulsions, which may be considered for bonding metals and cellulosic products. The commercial emulsions may contain 60 per cent of solids,

less than 1 per cent of unpolymerized vinyl acetate, and less than 0.3 per cent of acetic acid. They are compatible with chlorinated rubber and natural rubber latices<sup>47</sup>. Polyvinyl acetate emulsions are used commercially as adhesives for textiles, paper, leather, cork, metal, wood, etc. The bond is generally made by eliminating the water (about 55% solids) and curing under heat and pressure at 100 to 125°C. Zinc chloride or stannous chloride added to polyvinyl acetate emulsion is claimed to greatly increase bonding strength to metal<sup>47a</sup>. Small amounts of cupric dichromate will improve water resistance. Starch dispersing agents have been employed in emulsion polymerization of vinyl acetate at a pH of 3.8 to 4.9<sup>47b</sup>.

Adhesive sheets are also prepared by plasticization of the polyvinyl acetate with *p*-toluene sulfonamide-formaldehyde resins. When bonded to cellulosic sheets, these usually present a tacky surface<sup>48</sup>. Open-weave fabrics treated with polyvinyl acetate in acetone and alcohol form thermo-adhesive compositions<sup>49</sup>. By subjecting polyvinyl esters to the action of tannic acid, or by incorporating 6 per cent of its weight of tannic acid, their adhesive effect on paper, fabric, glass, or metal is improved<sup>50</sup>. Animal glue is also enhanced by a toluene solution of polyvinyl acetate and glycerol plasticizer. Emulsification is effected at 180°F<sup>51</sup>. Polyvinyl esters and condensation products of 1,3-butylene glycol and diglycollic acid have been prepared in the form of cast films, used as adhesives for veneers, fabrics, or safety glass<sup>52</sup>.

A very important commercial application of polyvinyl acetate adhesive is in the bonding of cellulose acetate sheet containing light polarizing crystals ("Polaroid") between faces of sheet glass<sup>53</sup>. Approximately 300 grams of polyvinyl acetate to 100 cc of dibutyl phthalate is the ratio of resin to plasticizer in the adhesive layer. A more recent development entails the molecular orientation of polyvinyl acetate with a trace of iodine, on stretching of the transparent sheet in one direction. This polarizer has been used in hundreds of thousands of military and civilian goggles<sup>53a</sup>. The polarizing polyvinyl acetate layer may be laminated to glass faces.

Coffman prepared a copolymer of 80 parts of vinyl acetate and 20 parts of divinyl formal with a softening point of 35°C<sup>54</sup>. Cheyney plasticized polyvinyl butyral with 2,2'-di-4-morpholinyl diethylamine<sup>55</sup>. In another adhesive development, films of polyvinyl acetate suited for safety glass were cut from cast blocks which had been frozen<sup>56</sup>.

Reviewing the art of polyvinyl acetate adhesives, then, one will find that they may be applied as:

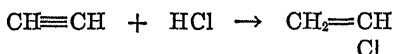
- (1) Solutions of polyvinyl acetate.
- (2) Hot melts, rendered adhesive by heat-sealing.
- (3) Emulsions in water.

They have given best results in applications to porous materials such as various cellulosic products, though their high initial tack has made them desirable in bonding various non-porous metals and glass. The loss of solvent and hence the development of ultimate strength is, however, very slow in these latter examples. The writer has found that the combination of polyvinyl acetate adhesives with thermosetting resin adhesives can benefit from the initial tackiness of the vinyl acetate polymers and the greater permanence of the thermosetting resins.

In formulations of the polyvinyl acetate solutions, ketones and hydrocarbons may generally be preferred for stability, with ethers, esters, and alcohols used less frequently. However, the wide choice of solvents is one of the features of polyvinyl acetate adhesives. If heavy film deposits are required, high solids content solutions or aqueous emulsions are preferred, though there may be equal justification in some problems for thin, low-viscosity solutions. In the final analysis, one should expect the retention of at least part of the solvent, unless forced drying is practiced.

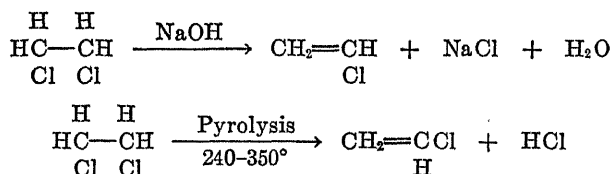
### Adhesives of Polyvinyl Chloride Acetate

Polyvinyl chloride has never been popular in the adhesive field, though there are interesting applications in its copolymerized form with vinyl acetate. Vinyl chloride, a gas, may be prepared by passing hydrochloric acid through acetylene gas, in the presence of a mercuric sulfate catalyst at 60 to 70°, as in the manufacture of vinyl acetate. An exothermic reaction ensues:



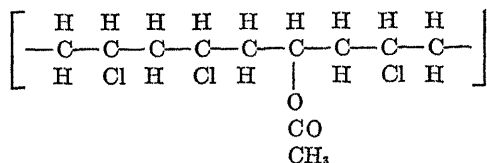
*Vinyl Chloride*

However, it may be formed also as a by-product in the manufacture of ethylene glycol, by the reaction of an alcohol solution of caustic soda upon dichloroethane. The presence of water aids the formation of ethylene glycol. Pyrolysis of dichloroethane in the presence of activated carbon will also yield vinyl chloride:



In the manufacture of polyvinyl chloride acetate, a copolymer, the simultaneous polymerization of vinyl acetate and vinyl chloride is practiced.

Polymerization is carried out in the presence of acetone, and the polymer is precipitated as a fine powder by the addition of water. Polyvinyl chloride is not readily dissolved by most organic solvents and is blended to various plasticizers with difficulty. The copolymer with vinyl acetate is, however, much more compatible; rigid and non-rigid sheets and molding compounds of polyvinyl chloride acetate are well known commercially. Most of these resins are high in vinyl chloride, usually better than 80 per cent, the 87 per cent vinyl chloride—13 per cent vinyl acetate combination being preferred for many applications. The copolymer is stabilized with various lead salts, such as lead stearate, particularly when it is to be exposed to higher temperatures. The copolymers are available in various molecular weights, up to approximately 20,000. The stronger, tougher sheets have the highest molecular weight and highest chloride contents, while lacquers and adhesive grades are formulated upon the lower molecular weights and higher proportions of acetate. The copolymer at 87 per cent vinyl chloride by weight has approximately nine vinyl chloride residues for each vinyl acetate residue in the chain. A portion of the copolymer may be illustrated as follows:



*Portion of Polyvinyl Chloride Acetate*

While polyvinyl chloride acetate has been widely used in the United States, its adhesive applications have not been nearly as widespread as in the case of polyvinyl acetate. The relationship between physical properties and molecular weight have been adequately described by Curme and Douglas<sup>57</sup>, while the differential weight distribution of the polyvinyl chloride acetate has been examined by Stoops and Douglas<sup>58</sup>. Fractions which are less soluble and are of higher molecular weights have better tensile strength and higher modulus of elasticity.

Polyvinyl chloride-acetate copolymers have attracted considerable attention in their plasticized forms, both as a rubber substitute and as coatings for water-proof cloth. Numerous equipments and textiles have been treated with these resins, as well as with plasticized polyvinyl butyral and polyvinyl chloride. The sheets may be bonded by sewing or cementing, or by heat-sealing. They are calendered on cloth or continuously extruded. Binocular coverings, electrical insulating sleeveings and tapes, conduit, and raincoats were among the many uses. A patent leather material widely used employs 85–97% vinyl chloride over 15000 mol. wgt. in the copolymer

and 20-45% plasticizer. This is laminated to a fibrous backing<sup>59a</sup>. Price described three types widely employed<sup>59</sup>:

Characteristics of Some Non-Rigid Polyvinyl Chloride Acetate.

Plasticizer (%)	30	35	40
Tensile Strength (psi)	2500	2000	1300
Ultimate Elongation (%)	300	330	350
Specific Gravity	1.23	1.20	1.18

The non-rigid varieties may be plasticized with such materials as tri-cresyl phosphate, dibutyl sebacate, dioctyl phthalate, and trioctyl phthalate. Their mechanical behavior over a range of temperatures have been investigated by Clash and Berg, who demonstrated the dependence of the low-temperature brittle point upon the plasticizers<sup>60</sup>. Duggan and Fligor examined the non-rigid polyvinyl chloride-acetate sheetings by creasing the sheets over a small radius<sup>61</sup>. Properties of films such as they found will also be applicable in part to the properties of the films employed as adhesives. They observed that the life of flexible polyvinyl resin sheeting is 30 to 200 times longer at 25° than at 0°. Press-polished sheets had two to three times the fatigue life of sheeting with a matte finish, and fatigue life increased very rapidly with plasticizer content.

The presence of plasticizers in the polyvinyl acetate copolymer sheeting should in general improve the bonding qualities of the sheet, providing the adhesive agent is readily compatible with the plasticizer. Otherwise the effect may be deleterious. Through the plasticizer, which should be mutually compatible with the adhesive agent and the polyvinyl resin, good cementing may be realized. The study of polyvinyl acetates and other thermoplastics to follow must include not only adhesives prepared directly from them, but also adhesive agents for them. In many instances the solvent-type adhesive may be best for bonding thermoplastic sheet materials.

One of the first applications of polyvinyl chloride acetate as an adhesive was described in its combination with Canadian balsam for use as an optical cement<sup>62</sup>. Reid reported that the copolymer of vinyl acetate and vinyl chloride possessed good adhesion<sup>63</sup>. Drukker points out that the first vinyl esters were made in this country in 1928, while in 1930 the copolymers of polyvinyl chloride acetate were introduced<sup>64</sup>. Young and Douglas indicated tetraethyl lead among the catalysts for vinyl chloride-vinyl acetate copolymerization<sup>65</sup>, while claims were made for the simultaneous polymerization of a vinyl halide with less than 30 per cent of vinyl acetate in plastic compositions<sup>66</sup>. Groff improved the adhesion of the polyvinyl chloride acetate to metal with a coumarone or alkyd resin<sup>67</sup>. Davidson prepared a resin compatible with nitrocellulose and soluble in various solvents through copolymerization of 70 per cent vinyl chloride and 30 per cent vinyl acetate<sup>68</sup>.

Adhesives for translucent films were prepared by combining polyvinyl chloride acetate and phenolaldehyde resins. They were dissolved in ethylene glycol or diacetone alcohol, and in some instances were blended with nitrocellulose. Solvent or heat was used to activate the surface for bonding<sup>69</sup>. Freyberg used polyvinyl chloride acetate for impregnating and cementing layers of fabric together. The general effect was to stiffen the fabric permanently even after laundering<sup>70</sup>. A small proportion of chlorinated rubber was found to aid the assembly<sup>71</sup>. This formulation contained a larger amount of vinyl acetate than in the other copolymers, 25 to 90 per cent being specified. Ushpol reported upon the use of polyvinyl chloride acetate in the shoe industry both as adhesive and impregnant<sup>72</sup>. More recent work indicates that laminates prepared from polyvinyl chloride acetate far outwear leather<sup>73</sup>. However, they still cannot be readily employed for the entire shoe (unless perforated) because they lack the moisture-transmission qualities of leather.

Polyvinyl chloride acetate resin coatings act as good adhesive layers in preventing the shattering of photoflash bulbs. A high degree of light transmission is important to such applications<sup>74</sup>. The coating and bonding together of fibrous bases with polyvinyl chloride acetate are aided with a plasticizing mixture of dibutyloxyethyl phthalate and butoxyethyl stearate. Calcium stearate is employed as a stabilizer<sup>75</sup>.

Campbell improved the adhesion of polyvinyl copolymers by including 0.1 to 4 per cent of maleic acid in the polyvinyl chloride acetate. No reaction with the polymer is claimed, though improvements are forthcoming<sup>76</sup>. The improved adhesion in this composition is attributed to the presence of unreacted carboxyl groups<sup>77</sup>. A highly important and versatile group of polyvinyl resin adhesives has been described<sup>78</sup>. Some of the resin adhesives require temperatures of 175° for baking, while others may be cured at lower temperatures. Shear strengths as high as 4000 psi are claimed for this material. The procedure of applying a prime bake coating is recommended, followed by low temperature-setting adhesive, if it is difficult to cure the assembly with heat.

Polyvinyl chloride acetate "organosols" represent a new development which may influence adhesive applications. A grade of the polymer has been prepared which does not require active solvents in the thinning agent. In this manner, coating materials of high solids content may be build up which can be readily applied to cloths and textile surfaces. The fine resin particles are ball or pebble-milled with low-cost thinners, pigments, and plasticizers for a number of hours and then applied to the cloth. A true solution of the resin is not effected. After the coating is applied, it is necessary to bake it at 175 to 180° to gain complete fusion<sup>79</sup>.

**Solvent Cements for Polyvinyl Chloride Acetate.** In general the cementing of rigid and non-rigid sheets of polyvinyl chloride acetate together

is best accomplished with the aid of various solvent cements. The choice and application of these cements are not nearly as extensive as with other materials, yet there are certain types which have given good results. The higher the chlorine content in the polyvinyl chloride-acetate ratio, the less effective is the solvent, and the more limited the choice. Ketones and some of the nitroparaffins are preferred groups from which solvents may be selected. Among the lower ketones, methyl ethyl ketone is more effective than acetone as a true solvent for some of the more readily dissolved polyvinyl copolymers. Nitromethane is also effective. Mesityl oxide, acetonyl acetone, methylisobutyl ketone, isophorone, and cyclohexanone are effective solvents for most of the polyvinyl chloride-acetate materials

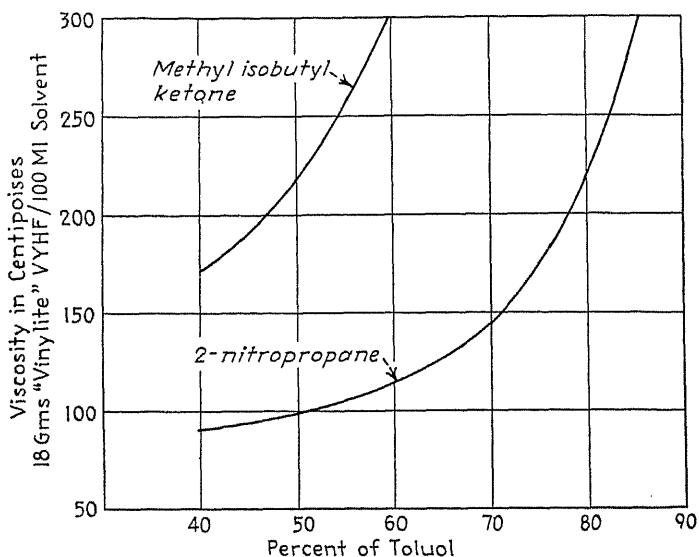


Figure 18. Viscosity concentration curves for "Vynlite-VYHF". (Courtesy Carbide & Carbon Chemicals Corp.)

and may be employed to bond them together. Tetrahydrofurane is also recommended as a solvent. However, the vapor pressure of some are low, and the removal of solvent from the glue line very slow. The variation of viscosity of polyvinyl chloride-acetate in toluene, ketone or nitropropane solvents is shown in Figure 18 for type VYHF resin<sup>80</sup>.

The more soluble types of polyvinyl chloride-acetate (Type VYNS for example) in solvents are sometimes prepared as adhesive solutions. In one typical formulation, 20 parts of polyvinyl chloride acetate, 32 parts of methyl ethyl ketone, 32 parts of cyclohexanone, and 16 parts of propylene oxide form the adhesive. A plasticizer such as dibutyl "Cellosolve" phthalate (Kronisol) is useful when there is a large concentration of fast-

evaporating solvents. The polyvinyl chloride acetate resins used in adhesives do not develop the high degree of tack that a polyvinyl acetate resin adhesive will, and for this reason it is sometimes desirable to incorporate acrylic and methacrylic ester resins, rosins, rosin esters, and coumarones<sup>81</sup>. A typical composition includes 10 parts of polyvinyl chloride acetate, 10 parts of poly-*n*-butyl methacrylate, and 80 parts of methyl ethyl ketone. It is also reported that some of the polyvinyl chloride acetate resins may be used with Hycar OR (acrylonitrile-butadiene copolymer) to formulate a pressure-sensitive adhesive which does not require an accelerator: for example, 10 parts of polyvinyl chloride-acetate, 10 parts of Hycar OR-15, and 80 parts of methyl ethyl ketone. Other adhesive formulations based upon synthetic rubber are recommended for the cementing of resin-treated cloth. In the manufacture of waterproof wearing apparel a liberal application of adhesives is to be preferred to stitching, which introduces openings through which water may leak. For porous surfaces such as wood or concrete, a primer coating of polyvinyl acetate is suggested.

Not to be overlooked is the possibility of heat-sealing fabricated assemblies of polyvinyl chloride acetate. Plasticized varieties bond very readily to one another in the presence of heat. However, it is important to confine the heat to the immediate glue line, inasmuch as plasticizer evaporation may cause a pronounced shrinkage. Strother lowered the fusion temperature of polyvinyl chloride acetate, without a reduction in hardness, by intimately mixing with pyrone<sup>82</sup>. Thin foils of polyvinyl chloride acetate are now being assembled by high frequency gluing techniques. A special machine resembling a sewing machine in appearance, produces seam welds in the resin sheet. Many useful applications of thin foils of polyvinyl chloride acetate are now made possible by this bonding technique.

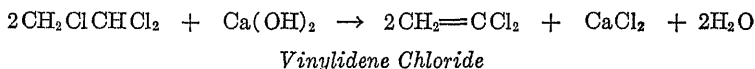
### Adhesives from Other Polyvinyl Copolymers

Besides polyvinyl chloride acetate, there are other polyvinyl copolymers which show promise as adhesives. Castor and Stoner describe a copolymer prepared from 80 per cent of vinyl chloride and 20 per cent of ethyl acrylate<sup>83</sup>. Partially polymerized alkyd resin added to this combination tends to adhere to the metal surface, while the vinyl resin concentrates at the air interface. In Germany copolymers of vinyl chloride and acrylic esters (Mipolam) resemble the polyvinyl chloride-acetate resins<sup>84</sup>. Safety glass adhesives have been prepared from vinyl cyanide and methyl acrylate<sup>85</sup>. A polyvinyl copolymer is also described as an adhesive and interlayer in safety glass manufacture<sup>86</sup>.

Also to be considered among the polyvinyl copolymers are polyvinyl chloride (approximately 90 per cent) and polyvinylidene chloride (10

per cent) known as the Geon resins. It is still too early to identify commercial applications of these resins as adhesives, though it is interesting to observe that a high solids, water-dispersed latex (50 per cent solids) has been prepared. The particles are said to be less than one-tenth micron in diameter. The latex is quite stable due to the small particle size and a protective colloid. Paper and fabric coatings possessing good bonding qualities have been developed. The specific gravity of the latex is 1.16; viscosity 10 to 15 centipoises; and surface tension 55–60 dynes per centimeter<sup>87</sup>. When it is blended with Hycar OR, very useful weather-resistant synthetic rubbers are obtained. Frictioned and coated fabrics offer much promise. In general, ketones are recommended as solvents<sup>88</sup>.

The other commercial polyvinyl copolymer of note contains a major proportion of polyvinylidene chloride and a small amount of polyvinyl chloride ("Saran"). Trichloroethylene and 1,1,2-trichloroethane reacted with calcium hydroxide at 90°<sup>89</sup>:



Polyvinylidene chloride is one of the most difficult polymers to dissolve, and while available in a number of important extruded products, its employment as an adhesive and as a coating are limited because of this lack of solubility. Hot solutions of ortho-dichlorobenzene (2 per cent solution) may dissolve the resin. A series of water dispersions of polyvinylidene chloride has been made available commercially. Solids content is as high as 60% with particle size of .08 to .15 micron. Various thickeners such as hydroxyethylcellulose and plasticizers, such as dibutyl phthalate in an emulsion form, are recommended in formulating the coatings<sup>89a</sup>.

### Halogenated Polyvinyl Chloride

The halogenation of polyvinyl chloride in a suspension or solution of carbon tetrachloride or tetrachloroethane leads to the formation of a polymer which is much more readily soluble in cheap lacquer solvents than polyvinyl chloride and of greater interest to the field of adhesives. In one process the polymerized polyvinyl chloride is chlorinated while suspended in a large amount of carbon tetrachloride. Methanol is added and the product filtered and washed. A chlorine content of 64 to 66 per cent is obtained<sup>90</sup>. The product is soluble to the extent of 20 to 30 per cent in butyl acetate, in mixtures of benzene and acetone, and in ethylene dichloride. Some depolymerization is also claimed for halogenated polyvinyl chloride, and adhesives for textiles, papers, wood, and safety glass are described<sup>91</sup>. This depolymerization also accounts in part for the improvement in solubility characteristics<sup>92</sup>. Methylene chloride is men-

tioned as a solvent for some of the adhesives, and leather applications appeared quite important<sup>93</sup>.

Combinations of halogenated polyvinyl halides and their depolymerization products with other adhesives are described by Menger as being particularly useful for leather products<sup>94</sup>. Wick discusses some of the details of halogenating polyvinyl halide in a solution of tetrachloroethane, which is chilled before adding methanol<sup>95</sup>. Menger describes cements being prepared from halogenated polyvinyl chloride as possessing good stability against water and also good flexibility. In one example of a leather adhesive, 22 parts of partially depolymerized chlorinated polyvinyl chloride and 4 parts of ethylacetanilide are dissolved in 47 parts by weight of ethyl acetate. Broad claims are directed to the use of this adhesive material<sup>96</sup>. Dimethyl phthalate is also employed as a plasticizer for this chlorinated resin.

Polyvinyl ethers are combined with halogenated polyvinyl chloride in some further developments<sup>97</sup>. Among other softeners mentioned for this resin are adipic acid and phthalic acid esters<sup>98</sup>. Further modifications and methods of preparation of chlorinated polyvinyl chloride are revealed by Evans<sup>99</sup>. The study of the good adhesive properties of halogenated polyvinyl chloride will indicate some of the reasons why polyvinyl chloride is not necessarily a good adhesive. The explanation may lie in relative proportioning of molecular weights.

### Polyvinyl Alcohol

A highly interesting polymer which has found some use as a water-re-moistenable adhesive material is polyvinyl alcohol. Vinyl alcohol has never been isolated, and polyvinyl alcohol is generally prepared from the hydrolysis of polyvinyl esters. Prepared by the alkaline hydrolysis of polyvinyl acetate, the product is light brown in color, though nearly colorless by the acid hydrolysis. Its manufacture from polyvinyl formate in an aqueous medium; using formic acid as a catalyst, is also described<sup>100</sup>. There is evidence that entirely different results are experienced in acid hydrolysis when compared with alkaline hydrolysis, the former method yielding hydroxyl and acetyl groups on the same chain. Saponification with alkali on the other hand, strips successive chains of their acetylation<sup>100a</sup>.

The solubility of the polyvinyl alcohol is dependent upon the residual number of acetate groups. Grades containing up to 5 per cent of alcohol groups are not readily soluble in cold water, while polyvinyl alcohol with up to 20 per cent of alcohol groups is partly soluble in cold water, and with 40 per cent of polyvinyl alcohol, is fully soluble in cold water<sup>101</sup>. The most important industrial reactions for polyvinyl alcohol are with aldehydes and ketones to form the polyvinyl acetals. The resins are usually made

available as fine white powders. It is quite a problem to grind these, though Irany describes a highly useful technique in which boric acid is reacted with polyvinyl alcohol or partially hydrolyzed polyvinyl esters. The tribasic boric acid is explained as forming spatially linked unstable polyesters with macromolecular polyvinyl alcohols<sup>102</sup>. They are converted into brittle, infusible masses on admixture of 2 to 5 per cent boric acid, rendering them suitable for grinding. After grinding the boric acid may be leached out with a few changes of water to restore the original polymer. The capacity of the borated resins to hold plasticizers dispersed as an internal phase is quite high.

Hermann and Haehnel were among the first to prepare polyvinyl alcohol by the hydrolysis of the polyvinyl esters<sup>103</sup>. Viscous aqueous solutions containing a few per cent of polyvinyl alcohol were employed as dispersing agents for dyes and sizings<sup>104</sup>, while its use as a safety glass interlayer were also proposed<sup>105</sup>. The addition of sugar or glycerol to polyvinyl alcohol has also been suggested as a material suited to the safety glass interlayer<sup>106</sup>. Polyvinyl alcohol or partial ester which dissolves or swells in water is employed for uniting materials containing cellulose or hydrophilic derivatives<sup>107</sup>. Schwartz suspended finely divided unswollen starch in an aqueous solution of polyvinyl alcohol (0.8 to 10 per cent). The ratio of starch to polyvinyl alcohol solution was 10:90 to 40:60<sup>108</sup>. These polyvinyl alcohol adhesives were quick-setting and applicable to paper, cloth, or cellophane. A good cellulose-to-cellulose bond was obtained with an aqueous solution of 3 per cent of polyvinyl alcohol and 30 per cent of unhydrolyzed starch (based on weight of polyvinyl alcohol). The mixture must be dispersed well.

In the manufacture of adhesive tapes, polyvinyl alcohol has been employed to join a layer of hydrophilic cellophane to a layer of hydrophobic rubber base adhesive<sup>109</sup>, though its water sensitivity will prevent its use as a sole bonding medium. As may be expected it will also secure hydrophilic layers to one another<sup>110</sup>. Tough, rubber-like adhesive products, soluble in acetone, are obtained by the reaction of acrylonitrile on polyvinyl alcohol at 50 to 100°, and in the presence of 1 to 10 per cent sodium hydroxide<sup>111</sup>. From one to several hours may be required for the reaction.

An adhesive paper has been prepared having on one side or surface a thin, dry, moistenable film consisting of polyvinyl alcohol<sup>112</sup>. The process has been carried further by building of tubular laminated structures of fibrous cellulosic materials, with the aid of polyvinyl alcohol as a bonding agent, and rolling pressure<sup>112a</sup>. A laminated structure bonded with the aid of polyvinyl alcohol has been described by Ford<sup>113</sup>. Polyvinyl alcohol has also been used in the manufacture of paper for photographic purposes, with the light-sensitive silver halide salt backed up by barium sulfate dispersed in polyvinyl alcohol<sup>114</sup>. In still another example, polyvinyl alcohol is

employed for its temporary binding qualities. Titanium dioxide crystals in a solution of polyvinyl alcohol are applied to a combustible base. The polyvinyl alcohol is decomposed and removed by heat, while the titanium dioxide fuses<sup>115</sup>.

In addition to polyvinyl acetate in the manufacture of light polarizing glasses, polyvinyl alcohol has also been used to orient the polarizing crystals, serving as the resin layer in a glass-bond-resin-bond-glass construction<sup>116</sup>. Molecularly oriented face sheets of polyvinyl alcohol have been also developed<sup>116a</sup>. Polyvinyl alcohol solutions have also been developed to protect metals which make contact with special solvents and lubricants<sup>117</sup>. Dangelmajer prepared a flexible, homogeneous plasticized polyvinyl alcohol composition, formable by heat and pressure without exudation and capable of heat-sealing<sup>118</sup>. Proportions indicated were polyvinyl alcohol, 100 parts; glycerin, 35 parts; water, 50 parts; and formamide, 5 parts.

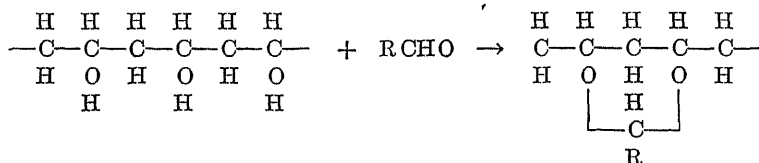
There have been a number of attempts to render polyvinyl alcohol waterproof to some degree, though elimination of swelling has not been accomplished. There are various ways to accomplish this result. Water-soluble secondary aromatic amine and a chloride of an amphoteric metal will increase the water resistance of polyvinyl alcohol<sup>119</sup>. Water-solubility can be reduced by a variety of chemicals, such as concentrated ammonium salts, aldehydes, chromium compounds, and dibasic acids<sup>120</sup>. As a water-soluble synthetic resin, polyvinyl alcohol is a rare example, and this quality often helps its application to coatings requiring water as solvent. Polyvinyl alcohol will also resist attack by bacteria and fungi. It has been plasticized with polyethylene glycols of high molecular weight<sup>120a</sup>.

### Polyvinyl Acetals

The polyvinyl acetals, which first began to enjoy commercial production in this country in 1937, were discovered in the late 1920's. The three best known materials include formaldehyde-modified polyvinyl alcohol, acetaldehyde, and butyraldehyde types. Many of these resins are tough and flexible, and exhibit good adhesive properties. Their development led to the application of polyvinyl acetals as the adhesive layer in automobile safety glasses, supplanting the earlier cellulose ester types. The polyvinyl acetals, particularly polyvinyl butyral, possess a high specific adhesion to glass surfaces, and do not necessarily require the presence of additional adhesive agents, as in the case of the interlayers of cellulose derivatives. While the applications of polyvinyl butyral to safety glass declined at the start of World War II, many new uses developed, particularly as a cloth coating and waterproofing material.

The properties of the polyvinyl acetals are dependent upon many factors,

including: (1) the molecular weight of the polyvinyl ester; (2) the degree of hydrolysis and substituent; and (3) the nature of the reactant. Correct applications of polyvinyl acetals depend upon the proper proportioning of the three components: polyvinyl ester, polyvinyl alcohol, and polyvinyl acetal, all of which may be present in varying degrees. Solubility and fusibility are dependent upon the nature of the aldehyde reactant. The simpler aldehydes such as formaldehyde yield the harder, less soluble compounds, while the higher aldehydes yield the softer polymers. In commercial practice, the starting point is polyvinyl acetate, and the polyvinyl acetal is the major component in the end of the reaction, polyvinyl alcohol formation being only an intermediary step<sup>121</sup>. The general reaction in the formation of the polyvinyl acetal may be shown as follows:



Polyvinyl Alcohol

Polyvinyl Acetal

The interaction of aldehydes and polyvinyl acetate was first recognized by a Canadian organization which obtained gummy resins in glass and aluminum vessels<sup>122</sup>. As a general practice freedom from dust or iron impurities is important to obtaining clear, colorless resins. The reaction is preferably carried out at elevated temperatures in the presence of catalysts such as hydrochloric acid or sulfuric acid<sup>123</sup>, or zinc chloride and aluminum chloride<sup>124</sup>. In the manufacture of formaldehyde-modified polyvinyl alcohol, the polyvinyl acetate may be reacted upon in the presence of acetic acid and sulfuric acid, followed later by formaldehyde. The product can be precipitated with water from the reaction. Higher molecular weight polymers are preferred for the polyvinyl butyral manufacture, which may be conducted in the presence of ethanol and sulfuric acid. Starck discusses a method of preparing the polyvinyl acetal by an emulsification technique, entailing the presence of polyvinyl alcohol emulsifying agent<sup>125</sup>.

Early recognition was accorded to the polyvinyl acetals both as lacquers and as adhesives<sup>126</sup>. The condensation products of aldehydes and partially hydrolyzed polyvinyl esters were dissolved in an organic solvent, and mixed with non-drying oils in another adhesive application<sup>127</sup>. In another modification of the formation of polyvinyl acetals, polyvinyl alcohol was treated with ether esters or diesters. The reaction was effected in solvents, and lacquer and adhesive applications are described<sup>128</sup>.

A new adhesive safety glass interlayer prepared from polyvinyl acetals was developed by Morrison<sup>129</sup>. Special cements were not necessary to

bind this resin to glass<sup>130</sup>. Low-temperature flexibility and high shock resistance made this safety glass interlayer superior to other types then available. It was also recognized early in the art that, by treating the polyvinyl polymers to increase the polar groups, the materials would adhere to glass surfaces with heat and pressure<sup>131</sup>. Reaction products of polyvinyl resins and aldehydes were prepared in an anhydrous solvent or acid to form formaldehyde- or acetaldehyde-modified resins<sup>132</sup>. Cellulosic materials have been bonded together by applying polyvinyl alcohol to the surfaces, adding aldehydes and catalyst, and acetalized *in situ*<sup>132a</sup>.

Much work has been done on the plasticization of polyvinyl acetals for use in safety glass construction, and dialkyl sebacates, such as dibutyl sebacate, found favor early in the art<sup>133</sup>. Polyvinyl acetal resins containing not more than 12 per cent hydroxyl groups and not more than 10 per cent ester groups were prepared under acid conditions to yield some interesting properties<sup>134</sup>. By combining more than one aldehyde (butyraldehyde plus formaldehyde or acetaldehyde) in the reaction, useful sheets for laminating purposes and adhesives were prepared. In addition, by suspending the polyvinyl resin in isopropyl alcohol or benzene, benzaldehyde and furfuraldehyde (less than 25 per cent) were reacted to form the acetal<sup>135</sup>.

In an excellent investigation of partial polyvinyl acetal resins, Reid indicated the best range for the selection of resins for laminating plate glass and for obtaining the best degree of adhesion<sup>136</sup>. Some of the data from his patent specification are reproduced in Figure 19. In Figure 19 the isothermal curves show how the softening temperatures of the polyvinyl acetal resins change with the degree and the kind of acetalization. Within the area encompassed by solid curve "A" on this chart are the ranges for the desirable compositions, with the most desirable formulations appearing within curve "B". The resins falling within curve "A" are described as soluble in alcohols and glycol monoalkyl ethers. Their outstanding characteristic, it is stated, is virtual insolubility in ester plasticizer at room temperature, though still with the capacity to absorb sufficient quantities to become soft. In Figure 19, curve "C" represents polyvinyl butyral acetalized 66 per cent and 31 per cent of plasticizer, while curve "D" represents polyvinyl butyral acetalized more than 85 per cent and 31 per cent of the same plasticizer. The high elongation and high tensile strength are apparent in curve "C". Stated numerically the preferred ranges of acetalization are as follows:

Acetaldehyde	85 to 94%
Propionaldehyde	52 to 92%
Butyraldehyde	42 to 82%
Valeraldehyde	33 to 62%
Hexaldehyde	31 to 45%

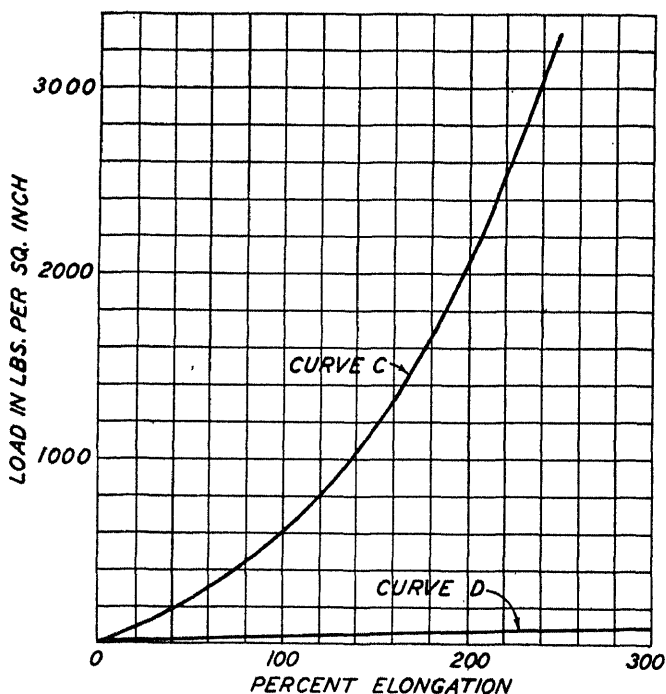
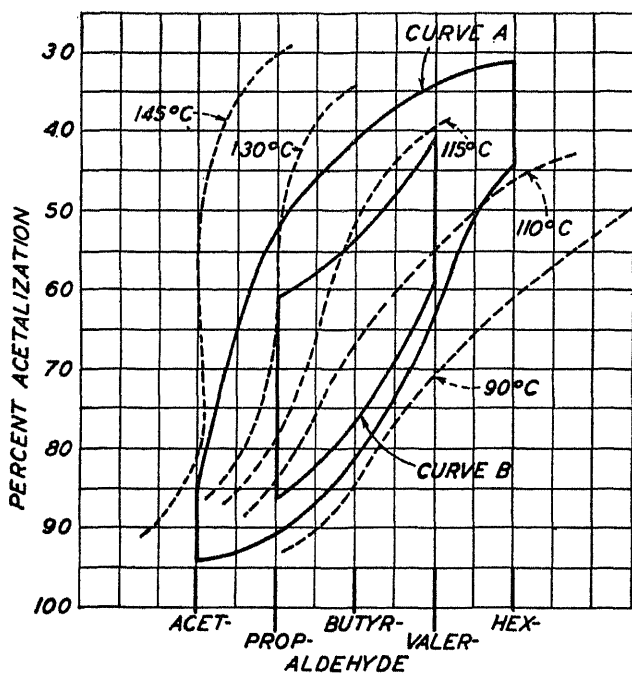


Figure 19. Influence of acetalization on softening point (above). Physical properties of polyvinyl butyral acetalized 66 per cent (Curve C) and 85 per cent (Curve D) (below). Data reference 136.

Ryan indicated a polyvinyl acetal with not more than 60 per cent of OH groups of polyvinyl alcohol, plasticized with an alkyl ester of a straight chain dicarboxylic acid<sup>137</sup>. Robertson confined the ranges of acetalization a little closer than Reid, indicating 54 to 78 per cent of hydroxy groups reacted with butyraldehyde, 62 to 88 per cent of hydroxy groups combined with propionaldehyde, and 39 to 58 per cent of hydroxy groups with valeraldehyde<sup>138</sup>. Morrison and Price indicate a preference for the acetal reaction to exceed 80 per cent. They also discuss the benefits from using alcohol as well as acid catalyst during acetalization<sup>139</sup>. Crane indicated polyvinyl butyral sheeting to have 0.5 per cent polyvinyl acetate, 19.0 per cent polyvinyl alcohol, 80.5 per cent polyvinyl butyral (70 per cent total) plus 30 per cent of dibutyl sebacate or triethylene glycol di-(2-ethyl butyrate).

Numerous plasticizers for polyvinyl acetal resins have appeared during the past several years. Nason and H. B. Smith suggested tributyl citrate<sup>140</sup>; H. B. Smith cited tetrahydrofurfuryl oxalate<sup>141</sup>; and Smith and Swan described other esters of tetrahydrofurfuryl alcohol<sup>142</sup>; Ryan recommended a diglycerol ester plasticizer<sup>143</sup>; Kyrides discussed neutral alkyl esters of diglycollic acid and thiodiglycollic acid<sup>144</sup>; Swan prepared rubbery sheets for safety glass from acetaldehyde modified polyvinyl alcohol and a mixture of dibutyl phthalate and dibutyl sulfone<sup>145</sup>; Kyrides included a dibenzyl or ditetrahydrofurfuryl ester of thiodiglycollic acid<sup>146</sup>; Izard preferred polyvinyl butyral plasticized with a monocarboxylic acid di-ester of octa-decanediol<sup>147</sup>; Craver employed two plasticizers, ethyl stearate and 1-alkyl amide (*n*-dibutyl lauramide)<sup>148</sup>; Keim mentioned the use of diethylene glycol dihexoate in a partial polyvinyl acetal for polarizing materials<sup>149</sup>; Land cemented his polarizing layers together with polyvinyl acetal plasticized with glycerol tri-ricinoleate<sup>150</sup>; Nason removed tackiness by including an alkylated diphenyl<sup>151</sup>; while Lycan employed a mixed ester of a glycol and two saturated aliphatic monocarboxylic acids<sup>152</sup>.

Polyvinyl acetal (100 parts) has been plasticized with 30 parts of diethylene glycol dipropionate and 30 parts of butyl carbitol butyrate<sup>153</sup>. Derby also specified a benzyl ether of diethylene glycol monopropionate and ethyl laurate<sup>155</sup>. Plasticizers from esters of polyalkylene glycol with caprylic and capric acid have made polyvinyl acetals strongly adherent to glass<sup>154</sup>. Carswell employed saturated quaternary ammonium hydroxide compounds such as the dimethyl dibenzyl and trimethyl benzyl ammonium hydroxide to stabilize polyvinyl butyral and improve its adhesion to glass in safety glass manufacture<sup>156</sup>.

Polyethylene glycol hexoate<sup>157</sup> and diethylene glycol dipropionate<sup>158</sup> are other examples of plasticizers for the polyvinyl butyral. The highly acetalized polyvinyl acetals have rather high softening points and must be

plasticized to acquire flexibility for many of their applications. One of the manufacturing problems in the use of the polyvinyl butyral sheets is the high specific adhesion they exhibit for one another, making it difficult to wrap them up as rolls. Powdered sodium bicarbonate liberally applied to the finished sheets reduces the tendency to stick together, and may be washed off at the time of assembly to glass plates. On the other hand, Crane suggests reducing the adhesiveness of polyvinyl acetal sheets by pitting the surface with a solvent, while the sheet is stretched under tension<sup>159</sup>. Paggi renders the surfaces non-adhesive by treatment with aqueous solutions of strong acid<sup>160</sup>.

A considerable amount of promise has been held for the mixed polyvinyl acetal sheet materials. McNally and Van Dyke prepared a number of mixed polyvinyl acetals containing less than 15 per cent of polyvinyl alcohol, less than 10 per cent of polyvinyl ester, and a polyvinyl acetal containing a variety of aliphatic aldehyde groups having not more than four carbon atoms<sup>161</sup>. Another example included a mixed polyvinyl acetal from benzaldehyde and an aliphatic aldehyde<sup>162</sup> and halogenated or nitrated benzaldehyde and aliphatic aldehydes<sup>163</sup>. An increase in flexibility without an increase in water absorption is claimed in these resins, which make them good photographic film carriers. Also mentioned is the possibility of impregnating fabrics and woods, and of laminating the same with these resins. Solubility in alkylene chlorides, and lower aliphatic alcohols and ketones is characteristic of the mixed polyvinyl acetals. A number of the resins are cast in thin sheet form from a solvent.

The polyvinyl acetals have had their solubility and thermoplasticity reduced through the introduction of phenol-formaldehyde resins into the laminating or coating varnishes<sup>64</sup>. On the other hand, dicarboxylic acids have been employed in the acetalization process to promote cross-linking between the hydroxyl groups on adjacent chains of polyvinyl alcohol and thus reduce swelling<sup>164</sup>. Blaikie and Crozier reacted an oil-soluble phenol-formaldehyde condensation (*p*-tert. amyl phenol) product with the polyvinyl acetal<sup>165</sup>. Polyvinyl acetals have also been employed to bond wood impregnated with urea-formaldehyde or phenol-formaldehyde resins<sup>166</sup>. Vidal specified polyvinyl acetals (butyral) for the manufacture of a number of his molded plywood aircraft structural elements<sup>167</sup>. The polyvinyl butyral was applied to the wood veneers by brushing or spraying, and the pieces assembled about the mold, which was then heated above 100°. Polyvinyl butyrals have tensile strengths of 1000 psi for the very soft stocks up to 3500 psi for the tougher stocks (elongations 400 and 200 per cent, respectively). Cements usually are formulated with ethyl or butyl alcohol solvents and some plasticizer. P.V. acetals have also been insolubilized by 2-3% glyoxals or methyl glyoxal.<sup>167a</sup>

Polyvinyl formal (formaldehyde modified polyvinyl alcohol) has also been employed in bonding wood veneers, particularly in the "Hydulignum" process for the manufacture of wooden airplane propellers<sup>168</sup>. A two-way compression is applied to obtain a highly homogeneous material of controlled density. Birch veneers  $\frac{3}{16}$  inch thick are coated with the polyvinyl formal resin, which was selected because of high softening point and absence of brittleness at the low temperatures. A specific gravity of 1.31 is obtained and a tensile strength of 45,000 psi is claimed.

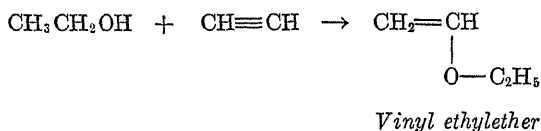
Polyvinyl acetals are also processed with rubber to yield a promising group of materials<sup>169</sup>. Aqueous emulsions of polyvinyl acetals will also be forthcoming. Aside from its employment as a flexible interlayer for safety glass, polyvinyl acetal resins and phthalate plasticizers have also been used as cements for cellulose acetate interlayers in safety glass<sup>170</sup>. Abrasive grains have also been bonded with a partial acetal of a vinyl ester resin<sup>171</sup>.

Bacon developed polyvinyl acetals adhesives for leather and cloth in the manufacture of shoes. Using polyvinyl butyral containing 16 to 22 per cent of hydroxyl groups or polyvinyl formal containing 8 per cent of hydroxyl groups, he combined the resin with dibutyl phthalate or dimethyl phthalate. It was claimed that a small amount of powdered copper (500-mesh), powdered aluminum (150-mesh), and nickel powder (150-mesh) present to the extent of 1 part per 100 of resin, arrested cold flow and creep in the glue line<sup>172</sup>. Burnt umber pigment and a chrome orange pigment also appeared equally effective in reducing cold flow.

The presence of ethyl silicate with a polyvinyl acetal is claimed as a good adhesive for a glass to wood bond, resistant to high humidities<sup>173</sup>. The ethyl silicate is partially hydrolyzed by refluxing in a mild acid. Glass fibers coated with a polyvinyl acetal resin are imbedded in a phenol-formaldehyde resin to be used in the manufacture of electrical insulation<sup>174</sup>. Bacon further specifies an inert inorganic pigment and polyvinyl acetal for bonding fibrous materials<sup>175</sup>. The heat resistance of the polyvinyl formal resins are improved by the addition of melamine-formaldehyde according to Swain and Adams, who combine the two resins with a molar excess better than 3 parts of polyvinyl acetal to 2 parts of the thermosetting resin. Improved heat resistance and chemical resistance are claimed<sup>176</sup>. Good adherence to metal surfaces is attained after baking at 135°. Useful blends of phenol modified coumarone-indene resins (up to 50 per cent) and polyvinyl formal have also been proposed as a new composition of matter. These compositions should have potential interest in the adhesives field<sup>177</sup>. Good adhesive properties are claimed when coatings are formed of polyvinyl formal which has been dissolved in 1,2,3-trichlorobutane<sup>178</sup>.

## Polyvinyl Ethers as Adhesives

The preparation of polyvinyl ethers may be conducted by reacting acetylene and an alcohol under pressure in the presence of a catalyst. Favorsky reacted an alcohol solution of potassium hydroxide upon methyl acetylene in a sealed tube and obtained a simple ether<sup>179</sup>; Plauson and Vielle conducted the reaction in the presence of mercuric sulfate catalyst<sup>180</sup>. Vinyl and other unsaturated ethers are produced from the contact of aromatic or aliphatic acetals with gold, silver, or platinum at 200 to 350°<sup>181</sup>.



Divinyl ethers may be prepared by reacting ethylene glycol and acetylene. It is reported that the production of vinyl ethers in Germany employed acetylene diluted with nitrogen, which diminished the reaction velocity<sup>172</sup>. A tabulation of some of the more important vinyl ethers follows:

Name	Boiling Temp. (°C.)	D <sub>4</sub> <sup>20</sup>	Refractive Index
Vinyl methyl ether	9-10	—	—
Vinyl ethyl ether	35-36	0.759	1.3856
Vinyl propyl ether	63-64	0.768	1.3902
Vinyl isopropyl ether	53-54	0.756	1.3840
Vinyl <i>n</i> -butyl ether	92-93	0.780	1.4015
Vinyl phenyl ether	153-156	0.977	1.5520
Divinyl ether of ethylene glycol	126-127	0.914	1.4340

The ethers are readily hydrolyzed into alcohol and aldehyde, though they may also be readily polymerized. Stannous and stannic chloride, aluminum chloride, and anhydrous strong acids have been employed as polymerization catalysts for the vinyl ethers<sup>183</sup>. The lower members such as polyvinyl methyl ether are water-soluble. Vinyl isobutyl ether polymerized with boron tri-fluoride at 10° or lower have formed the basis for some adhesives, particularly in safety glass manufacture<sup>184</sup>. Adhesive tapes, prepared with the aid of polyvinyl ethers applied to cotton, paper, or regenerated cellulose have been developed<sup>185</sup>. Copolymers of polyvinyl ethers prepared from aliphatic alcohols and other vinyl resins have also been made. In the presence of ammoniacal casein, one or more water-insoluble polyvinyl ethers of low molecular weight are prepared into an aqueous emulsion<sup>186</sup>.

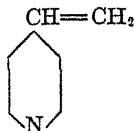
Reppe and Kuhn polymerized vinyl ethers in the presence of sulfur dioxide<sup>187</sup>, while iodine has also been found effective as a catalyst<sup>188</sup>. The

polymerization of the vinyl ethers does not proceed as readily as with other vinyl resins, and tends to form softer low molecular weight polymers. Polyvinyl ethers such as the methyl ether have also been combined with halogenated polyvinyl chloride<sup>97</sup>. Good adhesives for leather and for wood are obtained from a mixture of cellulose esters and polyvinyl methyl or ethyl ether, or mixed polymers with other ethers which are soluble in water-alcohol solvents<sup>189</sup>. As adhesives for paper and metal foil, they may be blended with paraffin and bitumen<sup>190</sup>. In the presence of salts of sulfonated fatty acids as emulsifiers, aqueous emulsions of polyvinyl ethers have proven valuable for wood, leather, textiles, and bonds to metals, it is reported<sup>191</sup>. Benzene, acetone or ester solutions of polyvinyl isobutyl ether are used for installation of upholstery in motor cars, cellophane foils, and in cementing to glass and metal.

Valuable adhesives for stoneware, porcelain, metal, glass and plastics are obtained by incorporating polyvinyl methyl and ethyl ethers into chlorinated polyvinyl chloride<sup>192</sup>. Additional plasticizers may be added such as phthalic or adipic acid esters. Divinyl ether has been produced from the action of solid KOH on dichloroethyl ether at 220° in an atmosphere of ammonia. It hydrolyzed in the presence of weak acids to acetaldehyde<sup>193</sup>. Beck patented a solution of polyvinyl isobutyl ether in benzene and acetone<sup>194</sup>.

### Miscellaneous Vinyl Resins

There are a few other polyvinyl resins worthy of note because of their potential interest in the adhesives field. One of these is polyvinyl pyridine which exists as a tough, elastic polymer. Its high cost at present precludes it from large-scale applications. Its structure is:



*Vinyl pyridine*

Particularly useful adhesive products are claimed from a solution of polyvinyl phenol. The vinyl phenols are produced by reacting phenol with a vinyl halide<sup>195</sup>. The vinyl ketones have also come in for some attention as adhesive agents. One useful method of preparation is based upon the hydration of monovinylacetylene, an intermediary product in the manufacture of chloroprene<sup>196</sup>. Ketones and aldehyde may also be reacted under carefully controlled alkaline conditions to yield a series of vinyl ketones. Polymerized phenyl vinyl ketones form colorless products of high viscosity. Their employment as a binding agent has been noted<sup>197</sup>.

Methyl vinyl ketone ( $\text{CH}_2 = \text{CH} \cdot \text{CH} \cdot \text{CO} \cdot \text{CH}_3$ ) has been made commercially available. Due to the rapid polymerization tendency, it is shipped as an azeotrope containing 15% water and a hydroquinone stabilizer.<sup>198</sup> When thermally polymerized, tough adhesives and flexible polymers are obtained.

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## Chapter 6

### Polystyrene and Acrylic Resin Adhesives

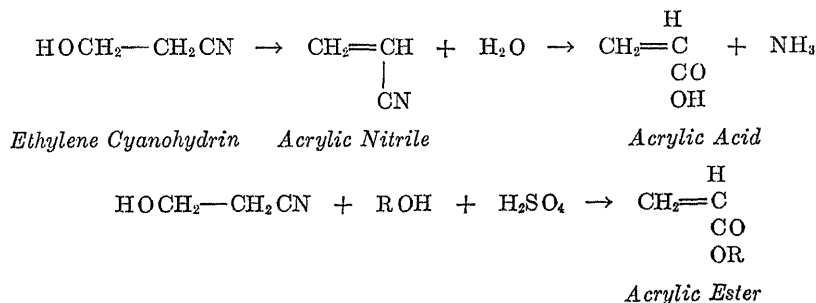
Among the noteworthy thermoplastics, polystyrene and esters of acrylic and methacrylic acid have been utilized in the preparation of adhesives. Although they are not employed as extensively as other adhesives, they warrant careful consideration in the future development of synthetic resin adhesives. Acrylic resins are best known as solid, transparent sheets of polymethyl methacrylate which have many applications as light-weight, tough, transparent enclosures. The fabrication and assembly of these transparent sheets through cementing entail special problems which are discussed in this chapter.

Polystyrene has not been as prominent in the field of adhesives as other thermoplastics; however, a few of its applications will be cited later in the chapter. In addition, attention will be directed to the more recently developed polydichlorostyrene, which displays better heat resistance than polystyrene. Both acrylic and styrene resin polymers are high molecular weight synthetic resins. While the higher and more complicated homologs of the acrylic resin series do not possess as high a degree of polymerization as the simpler members of the series; they are better known for their adhesive rather than cohesive properties. It is quite probable that better adhesives will be found among the softer, more tacky members of the acrylic resin series.

The unlimited possibilities of copolymerization should not be overlooked in a search for the optimum combination for adhesive purposes. Copolymers have already offered practical solutions to other plastics problems; for example acrylonitrile-styrene and ethyl acrylate-methyl methacrylate copolymers have demonstrated improved molding qualities over those offered by the pure polymer. In the development of softer varieties of acrylic resins, more satisfactory results are encountered through proper copolymerization than by plasticization. In this manner it is also possible to introduce side chains which may contribute to more efficient adhesion to specific surfaces.

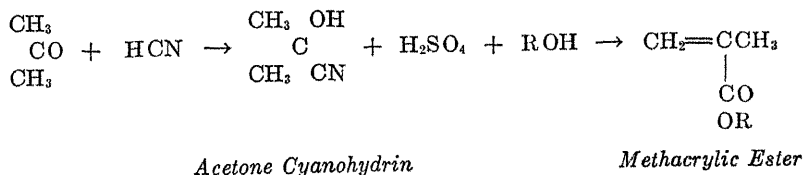
Early experimental efforts in developing acrylic acid revealed techniques for its preparation by the oxidation of acrolein. However, the acrylic acid esters investigated by Rohm in 1901, were the forerunners of the

present commercial polymers<sup>1</sup>. In the commercial preparation of acrylic acid and its derivatives, ethylene is reacted with hypochlorous acid giving ethylene chlorhydrin, which may be condensed with sodium cyanide to form ethylene cyanohydrin. By the elimination of water from the cyanohydrin, acrylic nitrile may be obtained, which in turn may be hydrolyzed to acrylic acid. On the other hand, refluxing together of ethylene cyanohydrin, an alcohol, and sulfuric acid, yields acrylic acid esters<sup>2</sup>:



Acrylic nitrile has also been manufactured by reacting HCN upon acetylene in the presence of a cuprous chloride catalyst<sup>3</sup>. Copolymerized with styrene, it forms the basis of an important molding compound. Fisher has also done considerable work recently on the preparation of acrylic acid and its esters by the pyrolysis of lactic acid to form methyl acrylate, and the alcoholysis of methyl acrylate to high acrylic esters<sup>4</sup>. A number of branch chain alkyl acrylates have been prepared from various primary and secondary alcohols. There is evidence that with increasing numbers of carbon atoms in the alkyl groups in the side chain, the brittle point of the resin is lowered<sup>5</sup>. Relatively high yields of acrylic acid are obtained by pyrolysis of the esters at 500 to 580°.

The esters of methacrylic acid are probably better known than those of acrylic acid. As in the case of the acrylic esters, dehydration of the cyanohydrin and esterification take place during the same reaction. Acetone and hydrogen cyanide are reacted together to give acetone cyanohydrin, which is treated with the appropriate alcohol and sulfuric acid for several hours:



The ester best known is methyl methacrylate obtained from the action of methyl alcohol upon acetone cyanohydrin. Other esters can be pre-

pared from higher ketones, though most of the interest has centered upon the acrylic and methacrylic esters. The acrylic esters polymerize more readily than the methacrylic esters. Conditions favoring polymerization are heat, light, and catalysts such as benzoyl peroxide. A number of emulsion polymerization techniques have been worked out to obtain the acrylic resins in a finely dispersed form. The monomer is treated with an emulsifying agent and catalysts such as peroxides, though in some instances vigorous stirring in the presence of various salts, e.g. talc, may bring about the result<sup>7</sup>. Solvents or plasticizers may also be present during emulsion polymerization; tetralin is effective in obtaining a slower controlled rate<sup>8</sup>. The prevailing pH will, however, greatly influence the physical nature of the polymer as it is formed, though many other agents will also affect emulsification<sup>9</sup>.

As for other synthetic resins, the nature of the solvent in which methacrylic esters or acrylic acid esters are polymerized will determine the average molecular weight. For example, Strain reporting on the polymerization of methyl methacrylate in solution indicated the following<sup>10</sup>:

Polymerization of Methyl Methacrylate in Solution<sup>10</sup>.

Solvent	Average Molecular Weight
Dioxane	35,000
Butyl acetate	41,000
Ethylene dichloride	54,000
Ethyl acetate	58,000
Acetone	75,000
Ethanol	75,000
50% Methanol	166,000

Generally, polymerization in mass results in higher molecular weight polymers when lower concentrations of catalyst are employed, or when the reaction is conducted at lower temperatures. To demonstrate the influence of the average molecular weight upon the physical properties, Staudinger and Trommsdorff<sup>11</sup> prepared a series of polymers of ethyl acrylate, and examined their properties. Ethyl acrylate is particularly desirable among the acrylic acid esters as an adhesive material. In the following data the molecular weight range where the best adhesive properties are apparent, should be noted:

Properties of Ethyl Acrylate Polymers<sup>11</sup>.

Molecular Weight	Properties of Polymers
2200	Viscous, colorless oil; dissolves easily in benzene
4000	More viscous than the preceding
7800	Tough, somewhat fluid; adheres to glass
14,500	Strong adhesion to glass; can be drawn into threads; slow dissolving in benzene
22,500	Tougher than preceding
41,000	Very tough, non-flowable
175,000	Tough, elastic, rubber-like

Neher described some of the characteristics of the other polyacrylates in the following manner<sup>12</sup>:

Properties of Polyacrylates<sup>12</sup>.

Polymer	Properties
Polymethyl acrylate	Tough, elastic
Polyethyl acrylate	Less tough, softer, elastic
Polybutyl acrylate	Soft, sticky
Polyisobutyl acrylate	Hard, crumbling
Poly <i>n</i> -hexyl acrylate	Soft, sticky

The properties of the polymethacrylate were evaluated by Strain and others. Some of the characteristics are reproduced in the following table:

Properties of Polymethacrylates<sup>13</sup>.

Material	Softening Temp. (°C)	Properties
Polymethyl methacrylate	125	Hard, tough
Polyethyl methacrylate	65	Tough
Poly <i>n</i> -propyl methacrylate	38	Tough, flexible
Polyisopropyl methacrylate	95	Solid
Poly <i>n</i> -butyl methacrylate	33	Flexible, tough
Polyisobutyl methacrylate	70	Brittle
Polylauryl methacrylate	—	Viscous liquid
Polyphenyl methacrylate	120	Very brittle
Polycyclohexyl methacrylate	105	Brittle
Polyglycol dimethacrylate	—	Not melting

Variations in the type of ester, degree of polymerization, and modification by copolymerization with two or more monomers will permit the attainment of a great variety of properties. In addition, the haloacrylates should also be considered. Marvel and coworkers observed that the *alpha*-haloacrylic acids and their derivatives are capable of polymerizing at room temperature, and in the presence of catalysts and ultraviolet light<sup>14</sup>. Strain and Pollack discussed the problems of obtaining clear, colorless chloroacrylate polymers, and recommended polymerization under anhydrous conditions. The presence of traces of water in the monomer or atmosphere sufficed to cause color forming bodies<sup>15</sup>.

Acrylic resins found early applications as adhesives in the manufacture of safety glass, forming an elastic film between the sheets of plate glass. The good adhesion of polymethyl or polyethyl acrylate to glass was a decided asset to the non-splintering qualities<sup>16</sup>, tending to hold broken glass fragments together. These acrylics did not go beyond limited experimental use as plastic interlayers in safety glass; they never approached the commercial status of vinyl resin for this purpose. Aside from their employment as plastic interlayers, sheets of polyacrylic resins have long been recognized as a glass substitute<sup>17</sup>. Polyethyl acrylate in acetone solvent was used for cementing papers or fabrics to metals<sup>18</sup>. The resin could also be made into sheets possessing good adhesive qualities. Water-

insoluble derivatives of acrylic or methacrylic acid were emulsified with various substances to form an artificial latex-like product which could be used as an adhesive<sup>19</sup>. Rohm proposed solutions of acrylic resins as coating and impregnating compounds, mentioning woods and fabrics<sup>20</sup>. Bauer discussed the general adhesive applications of polymerized acrylic esters and fillers, alone or with solvents<sup>21</sup>. Neher and Hollander critically examined the employment of acrylic and methacrylic acid esters in the manufacture of laminated safety glass<sup>22</sup>. As compared to the earlier developed cellulose derivatives, the discoloration in safety glass with acrylic resins was claimed to be negligible. Neher and Hollander prepared a number of interesting copolymers including esters of acrylic and methacrylic acid and vinyl ketone, or esters of itaconic acid, which found application in safety glass construction. Combinations of the two polymers prepared separately proved unsatisfactory. They recommended wetting of the acrylic resin surface with a plasticizing agent such as dibutyl phthalate, before bonding to the plate glass. Frederick demonstrated the acrylic interlayer in safety glass, and its ability to take much shock. No cements were used in sealing the acrylic interlayer to glass<sup>23</sup>, towards which it exhibited a good affinity.

The acrylic resins have also been employed as adhesives for other thermoplastics used as safety glass interlayers. Cellulose acetate coated with polyacrylic esters<sup>29</sup> or with polymerized acrylic acid<sup>30</sup>, was treated in this manner. It was found expedient to coat the glass surface with gelatin first, before applying the polymerized acrylic acid. It was suggested that assembly be completed in a bath of cyclohexanol containing dimethyl phthalate plasticizer. Adhesives particularly suited to the manufacture of safety glass were made by mixing polymerized methyl or ethyl esters of acrylic or methacrylic acid with cellulose tripropionate<sup>50</sup>. Only a limited compatibility could be expected in this combination.

Copolymers of acrylic resins have proven useful as adhesives for safety glass manufacture. Copolymers of acrylic esters and vinyl esters were proposed for this application<sup>31</sup>, as well as for attaching metal, glass, textile, and leather surfaces<sup>32</sup>. Kranzlein and also Hill specifically described vinyl acetate and acrylic acid esters for this use<sup>33, 37</sup>. Bauer and Gerlach tried mixtures of polymerized ethyl acrylate and methacrylate as safety glass interlayers. It has been generally recognized that the softer polymers possess superior adhesion for this purpose<sup>55</sup>. For best results in laminating glass, the solvent should be removed by forced drying, followed by moistening the film with plasticizer and assembling under heat and pressure.

Another technique for preparing safety glass was suggested by Rohm and Bauer who assembled two sheets of plate glass together with marginal

sealing strips of polymethacrylates<sup>51</sup>. The liquid resin monomer was then poured into the space formed between the two sheets and the polymer formed *in situ*. Considerable care must of course be exercised in heating large volumes of the monomer to avoid excessive exothermal heat and the appearance of bubbles. Especially clear castings are obtained with a sulfur dioxide catalyst<sup>52</sup>. Volumetric shrinkage during cure is alleviated somewhat by using polycyclohexyl methacrylate, which has a 12.5 per cent volumetric shrinkage during cure, as compared to the 22 per cent shrinkage of polymethyl methacrylate<sup>64</sup>.

Bauer investigated chlorinated polymers of acrylic acid and their derivatives, finding them suitable for lacquers, films, safety glass, and similar applications<sup>24</sup>. Acrylic acid, rather than its esters has seen much use as an adhesive, sometimes in combinations with dibutyl phthalate or glacial acetic acid<sup>25</sup>. The preparation of acetyl, lauryl, stearyl, allyl, and benzyl esters of methacrylic acid takes place by reacting  $P_2O_5$  with the ester of *alpha*-hydroxyisobutyric acid in an inert liquid<sup>26</sup>. Adhesive and coating applications of these esters are described.

Dittmar discussed the impregnation of wood with as much as 60 per cent methacrylic resin monomer, followed by polymerization *in situ*. In this manner the presence of large amounts of resin would enable the wood to resist warpage<sup>27</sup>. However, the presence of large amounts of thermoplastic resins in wood veneers, requires heating as well as cooling down in the press, and care must be taken in applying pressure in order to avoid excessive flow and hence splitting of the wood veneers, as in the preparation of plywood.

Acrylic acid esters prepared in emulsion have been employed as adhesives. A 25 per cent aqueous dispersion of methyl acrylate was polymerized in water in the presence of hydrogen peroxide, Turkey red oil, and sodium diisopropyl naphthalene sulfonate<sup>28</sup>. The polymer was produced in the form of a fine latex emulsion under these conditions. Mixed polymerization products of vinyl ethers with acrylic esters, amides, or nitriles have shown promise as binding agents and as coating materials<sup>24</sup>. Acrylic esters are also readily polymerizable with styrene in the presence of non-solvent liquids or in mass, and a peroxide type of catalyst<sup>35</sup>. Methacrylamide polymerized with vinyl esters or styrene are employed for safety glass interlayers or as adhesives. These interpolymers may be reacted further with aldehydes to form products useful as adhesives or molded products<sup>36</sup>.

Secondary or tertiary butyl or amyl alcohol esters of acrylic acid were deemed excellent adhesive materials when copolymerized with various vinyl esters or styrene monomer<sup>38</sup>. Water-soluble adhesives were prepared from 60 to 90 parts of vinyl methyl ketone and acrylic acid esters—

10 to 40 parts<sup>39</sup>. Sagel prepared a number of useful adhesives for organic plastics by mixtures of polymethacrylic acid esters with at least 3 carbon atoms in the alcohol radical, and 10 to 30 per cent of polyvinyl esters, phenolics, or nitrocellulose soluble in organic solvents<sup>40</sup>. Coes prepared various copolymers with ethylidene diacrylate and dimethacrylate by reacting ethylidene glycol with acrylic or methacrylic acid<sup>41</sup>. Styrene or nitrostyrene was copolymerized with these resins to form adhesive products useful for bonding abrasive grains. In bonding abrasive grains, Robie employed various acrylic acid ester polymers<sup>42</sup>. Lindh found hard adhering coatings when polymethacrylic esters had been copolymerized with 1 to 25 per cent of vinyl chloride and/or vinylidene chloride<sup>43</sup>.

In discussing aqueous dispersions of methacrylate esters and polyvinyl chloride esters, Renfrew and Flint described combinations of these, though in neither case were they the equal of rubber latex. Best films were formed by heating with infrared for one hour at 150°<sup>44</sup>. Fuoss and Mead conducted a number of electrical tests upon copolymers of acrylonitrile and ethyl acrylate, and pointed out that increasing amounts of the acrylonitrile gave harder and less flexible products<sup>45</sup>. Fisher and others copolymerized ethyl acrylate with small amounts of allyl maleate to obtain copolymers vulcanizable with sulfur. As little as 1 per cent allyl maleate introduced unsaturation from which cross-linking could be effected. Some of the rubber-like compounds prepared had tensile strengths of 1200 psi and elongations of 900 per cent<sup>46</sup>. Other acrylic resin copolymers have potential value in grinding wheels<sup>47</sup>.

The cementing of polymethyl methacrylate sheets has been accomplished with the aid of monomeric methacrylic acid<sup>48</sup>, or with the monomer of methyl methacrylate and 0.01 to 1 per cent of benzoin as a catalyst<sup>49</sup>. The latter may be cured by irradiation with ultraviolet light. In bonding sheets of clear polymethyl methacrylate it is claimed that the monomeric methacrylic acid has a solvent action upon the material, and that strong bonds which are craze-free are obtained in a much shorter period of time than with the ester in monomer form. A modification prescribes dissolving from one to five per cent of the polymer in the methacrylic acid monomer.

In another modification of acrylic resins, amino alcohols were reacted with acrylic or methacrylic acid to produce polymerizable esters especially suited for the bonding of wood<sup>56</sup>. Beta dimethylamino ethyl methacrylate and 2-diethylamino cyclohexyl methacrylate are mentioned in particular. Harmon also described tertiary amino alcohol esters of methacrylic esters, which are used as adhesives and as sizing agents<sup>57</sup>. Acrylic acid amides reacted with formaldehyde or its equivalent under neutral or slightly alkaline conditions may be employed directly as adhesives or

combined with mixtures or polyvinyl or polystyrene resins<sup>58</sup>. Barrett indicated that some of the amino alcohol esters of acrylic or methacrylic acid were prepared through interchange of alcohol radicals by heating a simple polymeric ester with an alcohol of higher boiling point, and distilling off the lower alcohol<sup>59</sup>. Other noteworthy esters were also produced by trans-esterification involving the Grignard complex<sup>60</sup>.

Interpolymers of 30 to 98 per cent methacrylic acid with 2 to 70 per cent methyl methacrylate are valuable for bonding and stiffening fabrics<sup>61</sup>, though polymethyl methacrylate may be used alone<sup>62</sup>. Synthetic rubber products have also been obtained through interpolymerization of acrylonitrile with butadiene (Perbunan or Buna N or Hycar) as well as by interpolymerizing methyl methacrylate with butadiene<sup>63</sup>.

Freydberg developed a composition for laminating cloth and stiffening fabrics from 100 parts of methacrylic acid, 10 parts of dibutyl phthalate, and 10 to 40 parts of chlorinated rubber<sup>65</sup>. Adhesives prepared from other acrylic acid derivatives have been employed for laminating fabrics together and rendering them gasproof. Polymers of beta ethoxyethyl methacrylate dissolved in toluene have been used for this purpose<sup>66</sup>. Acrylic acid or methacrylic acid polymers are also used as shoe stiffeners<sup>67</sup>.

Mitchell developed non-solvent type of adhesives from methacrylate polymers, including cyclohexyl methacrylate, butoxyethoxyethyl methacrylate, isobutyl methacrylate, methoxyethyl methacrylate, and *beta*-morpholine-amino-ethyl methacrylate. The resins were polymerized *in situ* at the point of application<sup>68</sup>. The problem was directed towards the bonding of non-fibrous cellulosic sheets such as cellophane. They were particularly effective on waterproof types which were protected with wax, because the above high-boiling polymerizable liquids have a solvent action on the wax. To improve the initial tack of such compositions, cellulose derivatives may be added. In one example of laminating adhesive for regenerated cellulose, the following proportions were cited:

	Parts
Ethylene glycol monoethyl ether methacrylate monomer	50
Nitrocellulose (Type RS)	3
Hydrogenated ester gum	5
Benzoyl peroxide	.5
Paraffin wax	.5
Dibutyl phthalate	1

Zimmer and Morway employed acrylic polymers to improve the adherence of greases to metal surfaces which were in motion. To oils ranging from 35 to 5000 seconds Saybolt viscosity are added 5 to 15 per cent of sodium, calcium, or aluminum soaps plus esters or ethers of acrylic or methacrylic esters. Preference is expressed for highly polymerized (30,000

to 200,000) oil-soluble linear acrylic polymers such as lauryl or cetyl methacrylate. Hydronaphthalene is mentioned as solvent for these polymers<sup>69</sup>.

Kuettel discussed the problems of producing a proper bond between polyvinyl butyral sheets and polymethyl methacrylate, pointing out that several hundred types were tried before a satisfactory one was obtained<sup>70</sup>. Sheets of acrylic polymers with an interlayer of polyvinyl butyral have been successfully used as the shatter-resistant, and in some cases self-sealing transparent enclosures used on high altitude bombers, such as on the B-29 airplane.

Building elements of polyvinyl or polyacrylic resins are joined to one another by heating the joint with hot air to the melting point and then pressing the elements together<sup>71</sup>. This assembly method gives strong joints, though practically it is limited to relatively small strips or areas being bonded. Lindh and Phillips practiced the same idea of using hot gases to heat weld miscellaneous thermoplastics<sup>72</sup>.

There is considerable merit to the heat welding of thermoplastics and its specific application to the bonding of polymethyl methacrylate sheets. Strength values approximate those of the original sheet, something which the best solvents have not been able to do with the same good clarity. The writer has found that the best technique is to heat the surfaces to be welded to high temperatures, until there is some localized decomposition as evidenced by bubble formation and localized boiling, and then to press the parts together so that the softened portions are squeezed out at the edge of the glue line. This excess may be sanded or machined off and after polishing there should be no trace of the glue line to the eye, unless viewed with the aid of polarized light. Instead of applying heat by hot gas, a heated stainless steel polished strip may be pressed against the surfaces to be joined and temperatures may be observed with the aid of a thermocouple; the best range for acrylics is around 320 to 370°. Stephen recommended slow cooling during heat welding to alleviate internal strains<sup>73</sup>, while Delmonte illustrated the heat welding of acrylic rods<sup>74</sup>. Electrically heated jigs may also be designed to effect heat welding of polymethyl methacrylate sheets or other thermoplastics, though the cost of such units is only justified by large production requirements.

Another modification of heat welding is resistance welding, where a rotating part can generate heat by friction. This followed by firm pressure bonds the parts.

### Solvent Cements for Polymethyl Methacrylate

Polymethyl methacrylate transparent sheets are widely used in the fabrication of many attractive articles; a few representative ones are shown in Figure 20. Much time and effort has been spent in developing

clear, transparent adhesives for these assemblies and some measure of success has been achieved. However, the problems are many, magnified largely by the transparency of the materials which will permit visual inspection of every little flaw and bubble in the glue line. Such imperfections in the joints may be caused by gas or vacuum pockets, as well as crazing. Crazing, which results in minute cracks scattered over the surface, is largely brought about by the combined presence of physical stress and solvents. As a matter of fact, the development of craze marks may be employed to indicate the magnitude of the stress present on the surface, because the frequency and concentration of craze lines are indicative of this. Best results will be obtained when cementing upon stress-relieved surfaces or surfaces with no previous history of severe stressing.

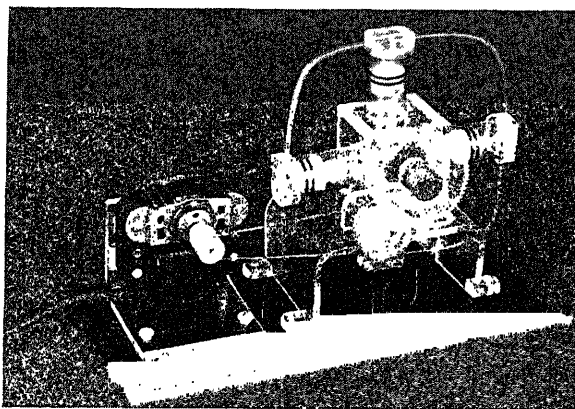


Figure 20. Small model pump. Fabricated parts cemented together by solvent cement.

Polymethyl methacrylate has numerous solvents which may be successfully used for cementing purposes, with chlorinated hydrocarbons among the more popular ones. The general technique requires wetting the surface thoroughly with the solvent to permit the sheet to soften, and then pressing the surfaces to be joined firmly together. In order to avoid having the solvent run off the glue line and damage the appearance of the rest of the sheet, some masking tape or film, such as polyvinyl alcohol, may be used to confine the action of the cement to the glue line. Among solvent cements which have been tried are the following; they may appear in various combinations:

Ethylene dichloride	Chloroform
Vinyl acetate monomer	Methyl methacrylate monomer
Methylene dichloride	Glacial acetic acid

In addition to the above, the writer has found both furfural and furfuryl alcohol to be very effective solvent cements for the polymethyl metha-

crylate. The darker color of these cements is not very apparent as a thin glue line. In one group of experiments to determine the effect of increasing hydroxyl groups upon the strength of the glue line, small amounts of maleic anhydride were dissolved in the furfural before application; no improvement in strength value was realized. To demonstrate the increase in strength of the glue line as a function of time of exposure at room temperature, the data shown in Figure 21 represent shear strength as obtained by a three block shear method. It is quite apparent that the presence of solvent, while important to the initial tack and adhesiveness of the assembly, is nevertheless detrimental to the ultimate strengths which may be obtained.

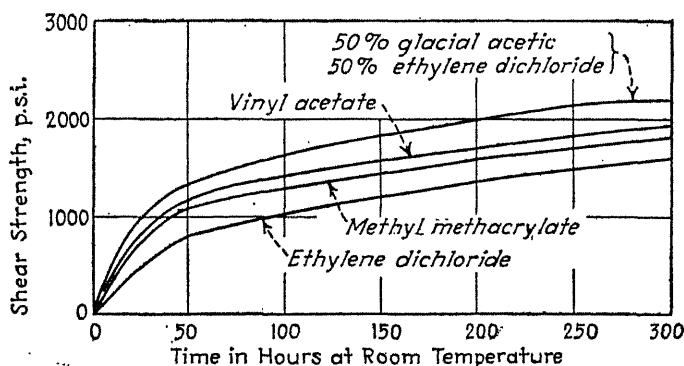


Figure 21. Increase in shear strength of  $\frac{1}{4}$  inch acrylic sheet at room temperature for different solvent cements.

The use of colored cements in the assembly often lends a decorative touch to transparent acrylics. A light blue or red glue line, or even a dark black line will bring about interesting composite laminates. The writer has prepared assemblies of ceramic bricks with acrylic sheets cemented to them at the glue lines, giving the over-all effect of a semi-transparent wall.

Solutions of polymethyl methacrylate in solvents are sometimes useful for adhesive purposes, though primarily in bonding other types of materials such as porous cellulosic substances. Strain evaluated the viscosity of polymethyl methacrylate in various solvents; he pointed out that the least viscous solutions are obtained with 22 per cent methanol and 78 per cent toluene<sup>75</sup>.

Viscosities of 15 Per Cent Polymethyl Methacrylate Solution<sup>75</sup>.

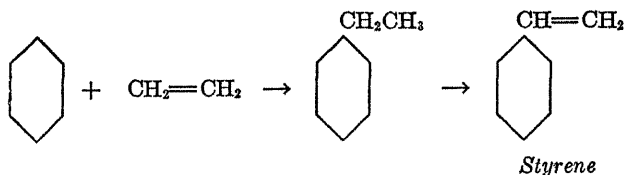
Solvent	Viscosity at 25° (cps)
Toluene	380
Ethylene dichloride	900
Acetone	2000
Dioxane	2200
Ethyl Acetate	4000

The viscosity of other polymethacrylate esters at 25° is shown in a paper by Strain, Kennelly, and Dittmar<sup>76</sup>. The greater solids content possible with the higher polymethacrylate esters is apparent from their data. As a general purpose adhesive comparable to, for example, polyvinyl acetate, the softer polymers should be considered. While various ester type plasticizers may be used with the acrylic resin polymers, it is generally preferred to employ a softer polymer or a copolymer developed for the purpose intended. Another factor to be considered in cementing acrylics and other thermoplastics, is the preconditioning of the material, as in some cases the presence of appreciable amounts of moisture on the surface will adversely affect the strength developed.

### Polystyrene Resin Adhesives

In spite of the wide scale use of styrene by the rubber industry and in the manufacture of molding compounds, the number of adhesive applications have been relatively few. The development of tremendous styrene production capacity (some 200,000 tons) for the manufacture of synthetic rubber makes available a raw material, which will serve as a focal point for many new developments. Attention has already been called to the role of partially polymerized or monomeric styrene in combinations with various polyesters for laminating purposes.

Ethylbenzene, prepared from the reaction of benzene on ethylene in the presence of aluminum chloride<sup>77</sup>, is cracked at high temperatures to yield styrene:



The pyrolysis of ethylbenzene may be conducted at high temperatures in an iron tube though the yields are not too high. Preference has been expressed for pyrolyzing ethylbenzene with superheated steam at 800 to 950°<sup>78</sup>. Another procedure is to chlorinate ethylbenzene and then react with alkalis, though chlorinated by-products are formed by this method. Styrene, boiling point 145–147°, is a clear colorless liquid which is made available commercially with at least 98 per cent purity. The presence of impurities leads to discoloration and sometimes unstable products.

Polystyrene is one of the oldest synthetic resins, having been prepared over 100 years ago by Simon<sup>79</sup>, who transformed the liquid styrene to its polymer. Much credit must go to Matthews for calling attention to the properties and potential applications of polystyrene<sup>80</sup>. He also produced

polystyrene by contact of styrene with a sodium metal catalyst. Polystyrene was first introduced into this country from abroad as a coating material (Victron). As improved methods for its manufacture were worked out, other major uses were developed, and from 1937 wide scale applications were known. Polystyrene may be cast into thin films useful for electrical insulating and laminating purposes, for example, in the manufacture of small condensers. The disadvantage of polystyrene films is their brittleness, which has been overcome in part by stretching lengthwise and broadwise at high temperatures and then cooling while stretched<sup>81</sup>. Polystyrene foils rendered pliable by heating have been recommended as adhesive foils for the bonding of wood veneers<sup>82</sup>. Various efforts have been made to manufacture a cellulosic tape impregnated with polystyrene because of its good dielectric properties. The impregnation of porous cellulosic products with styrene resin monomer offers no difficulty, though problems arise when polymerizing styrene *in situ* at temperatures of 130 to 140° when substantial volatilization takes place. In one instance of preparing styrene impregnated tape, heating to polymerize was conducted in an inhibited styrene bath to prevent volatilization<sup>83</sup>. In another example, fibrous tape impregnated with a mixture of polystyrene and monomer styrene (10 to 50 per cent) was employed as electrical insulation. The sticky tape which was formed hardened upon the polymerization of the monomer. Polystyrene may be dissolved in its monomer<sup>84</sup>.

Adhesion of polystyrene coatings is said to be improved by the addition of 10 to 25 per cent of cumarone resin. A coating containing these resins as well as tricresyl phosphate was used to finish terrazzo floors<sup>85</sup>. A useful varnish was prepared by Ostromislensky, who employed a small amount of rubber and styrene monomer in xylene. Polymerization was conducted at 135 to 140°<sup>86</sup>. Various lacquers and adhesives have been made from solutions of copolymers of styrene and maleic-anhydride which are soluble in acetone<sup>87</sup>. Styrene or vinyl esters were also copolymerized with maleic anhydride or fumaric acid to form adhesives and lacquer coatings<sup>88</sup>. Staudinger showed that small amounts of divinyl benzene copolymerized with styrene will lead to cross-linking which reduces swelling in the presence of solvents<sup>89</sup>.

The binding qualities of polystyrene as well as its good electrical insulation were combined in an application to compressed magnetic powder cores used in telephone loading coils<sup>90</sup>. Condensation products were also prepared by reacting phenol and styrene in the presence of iodine and  $\text{CCl}_4$  and treating with paraformaldehyde in the presence of stannic chloride. The end products were employed as adhesives and lacquers<sup>91</sup>. Melamine formaldehyde and polystyrene were combined in another application to form coatings with high temperature resistance and good electrical proper-

ties<sup>92</sup>. In preparing the melamine formaldehyde for this combination the molar ratio of formaldehyde to melamine was at least 4 to 1, though this resin comprised less than 40 per cent of the total.

Cummins and Bacon prepared a number of thermoplastic pressure sensitive adhesives based upon polystyrene<sup>93</sup>. Using 15 to 40 per cent polystyrene and 60 to 85 per cent triaryl phosphates, solutions of 25 to 300 centipoises viscosity were obtained at 60°. Di-*o*-xenyl monophenyl phosphate and diphenyl mono-*o*-xenyl phosphate were mentioned in particular. The resin coatings were applied at 120 to 200° to various cellulose derivative tapes, without solvents. The triaryl phosphates are non-volatile, colorless, and compatible with polystyrene. Abrams and Forcey also suggested the use of polystyrene in pressure-sensitive adhesive tapes<sup>94</sup>.

Other electrical insulating tapes made of plasticized polystyrene were prepared by Ford and New, who impregnated at least 45 per cent plasticized polystyrene into a fibrous backing at an elevated temperature<sup>95</sup>. Polystyrene adhesives have also been allocated to replace a part of the rubber adhesives in the manufacture of shoes<sup>96</sup>. Metal parts of an electrical fitting have been sealed to ceramic parts with the aid of styrene polymerized *in situ*<sup>97</sup>.

Considerable promise is held for dichlorostyrene, which exhibits better chemical resistance and considerably better heat resistance than polystyrene. Molding compounds prepared from these materials have ASTM heat distortion above that of boiling water. The possibilities of these materials as adhesives have also been mentioned<sup>98</sup>. Various isomers have been prepared from dichlorobenzaldehydes. Monomeric dichlorostyrene is much more active than styrene and will set up much more rapidly. A comparison of their properties shows the following:

Comparison of Properties<sup>98</sup>.

	Polydichlorostyrene	Polystyrene
Compression Molding, F°	350-425	275-375
Injection Molding, F°	475-525	325-500
Impact Strength, ft lbs/in notch	1-1.5	.26-.40
Heat Distortion, F°	240-265	165-190
Specific Gravity	1.39-1.40	1.05-1.70

Various copolymers have also been prepared with dichlorostyrene including acrylics, styrene, butadiene, isoprene, maleic anhydride, etc. Molding applications of polydichlorostyrene ("Styramic HT") have also been described by Jones and Brown<sup>99</sup>. Various copolymers were prepared of *p*-chlorostyrene and methyl methacrylate, vinyl acetate, dimethyl fumarate, and dimethyl maleate by Marvel and Schertz<sup>100</sup>. Britton and Le Fevre also prepared copolymers of *p*-chlorostyrene and unsaturated ethers or esters containing at least two unsaturated linkages<sup>101</sup>.

The chlorination of carbon tetrachloride solutions of polystyrene yields interesting chlorinated polymers which have good heat distortion points and excellent chemical resistance. The chlorinated polymer precipitates from the solvent after two chlorine atoms have attached themselves to each monomeric unit. Low temperature chlorination in the presence of iodine appears to give the best results.

Aside from the chlorinated polymers, polystyrene may have its heat resistance improved through various chlorinated biphenyls and appropriate fillers. For example, 30 to 60 parts of decachlorobiphenyl and powdered mica are blended with 100 parts of polystyrene<sup>102</sup>. Various catalysts will influence the polymerization rate of styrene; benzoyl peroxide and stannic chloride are mentioned most frequently. The latter gives darker colored end products of lower molecular weight, though the reaction may be carried out at a lower temperature. A systematic study has been made of the copolymerization rates of styrene and methyl methacrylate<sup>103</sup> in the presence of various catalysts. Chain growth processes by free radicals appeared substantially correct.

While polystyrene is not compatible with cellulose esters or ethers, it may be copolymerized with a number of thermoplastic synthetic resins to obtain useful polymers. Up to 5 per cent of acrylonitrile will, for example, improve its heat resistance<sup>104</sup>, while important combinations with vinyl esters and ethers have been noted<sup>105</sup>.

The molecular weight of the commercial molding grades of polystyrene resin is in the range of 65,000 to 95,000, while some grades have an average of 125,000. Much higher and lower molecular weight have been obtained in the laboratory, though the types developed are best suited for molding purposes, having good mechanical properties.

The fact that there are numerous solvent cements for polystyrene is an important consideration when blending it with other ingredients. Acetone, chloroform, ethylene dichloride, toluene, benzene, butyl acetate, and carbon tetrachloride all are effective solvents which will readily soften the surface of polystyrene and promote good bonding. On the other hand, various simple aliphatic alcohols have no effect whatsoever upon polystyrene and hence are not used. Polystyrene parts may also be heat welded, as were the acrylics, except that lower temperatures would be used for polystyrene sheets, which soften more readily.

Polystyrene resin emulsions may be prepared quite readily with the aid of suitable emulsifying agents and procedure. Benzoyl peroxide and sodium perborate, both water-soluble, and monomer-soluble catalysts may be added, as well as ammonium oleate as an emulsifier. Sulfonates or albuminous substances may also be used to prepare a polystyrene emulsion, while the addition of methanol will cause separation of the powder which

is easy to wash and to dry<sup>106</sup>. Copolymerization may be carried out with the reactants in an emulsified state. Mark and co-workers recently studied the mechanism of the emulsion polymerization of styrene<sup>107, 108</sup>. The effect of catalyst concentration and concentration of the emulsifying agent were qualitatively evaluated. Molecular weights were determined after different periods of polymerization through measurements of viscosity in toluene. It was observed that all emulsions underwent a drastic drop in average particle size during polymerization. Also of interest was the influence of ammonium oleate concentration on the average particle

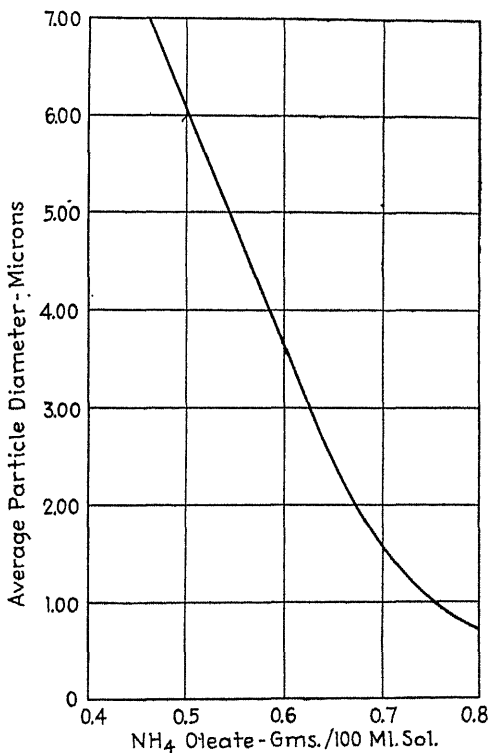


Figure 22.

Influence of emulsifying agent on particle size of polystyrene produced by emulsion polymerization (108).

size (see Figure 22)<sup>108</sup>. A typical solution comprised 180 grams of water, 19 grams of styrene, and 2.8 grams of sodium perborate.

Emulsions of polystyrene as well as the acrylic resins possess value as impregnants and coating materials, and are capable of developing high solids contents without an excessively high viscosity. The importance of adhesive films from these emulsified coatings should not be overlooked.

Polystyrene has also been applied as an adhesive in the bonding of cellulose esters and sheets of glass in safety glass manufacture<sup>109</sup>. Grinding wheels have been cemented with the aid of plaster of Paris, polystyrene,

and a solvent<sup>110</sup>. Polystyrene has been used as a waterproof bonding agent in abrasive cloths and papers<sup>111</sup>.

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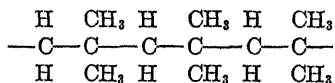
## Chapter 7

# Adhesives from Miscellaneous Thermoplastic Synthetic Resins

The majority of all thermoplastic synthetic resins have been proposed at one time or another for application as adhesive materials; a few of these are exceptionally outstanding. A number of thermoplastic resins which were not covered in preceding chapters will be reviewed in the following pages. These synthetics have not enjoyed the wide-scale analysis and interest which have been accorded to other types; however, their qualities should merit much attention in future trends of the adhesive field. The types of resins to be discussed here include polyisobutylenes, polyethylenes, coumarone-indene resins, and polyamides.

### Polyisobutylenes

Considerable quantities of isobutylene may be obtained from cracked petroleum, and when polymerized, form a number of interesting compounds ranging from oily substances of low molecular weight to rubber-like polymers of high molecular weight. Although they are essentially derived from isobutylene, they are prepared commercially from isobutylene containing various percentages of the *n*-butenes<sup>1</sup>. Molecular weight determinations are generally predicated upon Staudinger's viscosity method, and  $K_{cm}$ , the molecular weight concentration constant in tetrahydronaphthalene is  $.77 \times 10^{-4}$ . The structure generally ascribed to polyisobutylene is:



*Polyisobutylene*

While liquid products of relatively low molecular weight have been prepared from isobutylene and known for some time<sup>2</sup>, products of relatively high molecular weight are of more recent origin, ranging from 2000 to 10,000<sup>3</sup> and even considerably higher<sup>4</sup>. The polymerization of isobutylene at low temperatures with acidic catalysts takes place with explosive violence<sup>5</sup>. An almost quantitative yield takes place within a fraction

of a second. Aluminum chloride and stannic chloride have been used as catalysts, but best results appear to be obtained with boron tri-fluoride ( $\text{BF}_3$ ) as catalyst. The molecular weight of the poly-isobutylene is markedly dependent upon the temperature as well as the purity of the isobutylene. Results of Frolich and others<sup>4</sup> are reproduced in Figure 23, which shows the relationship between molecular weight and reaction temperature, the highest values (over 100,000) being produced below  $-80^\circ$ .

Diluents are employed to moderate the violence of the reaction<sup>6</sup>, causing an average molecular weight increase to approximately 80 per cent by volume of the diluent; above this point there is a rapid drop in average molecular weight. A number of interesting adhesive applications have

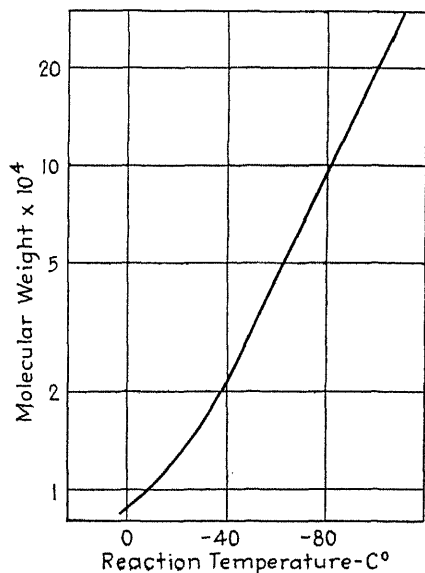


Figure 23.  
Relationship between molecular weight and reaction temperature in polymerizing isobutylene. (Frolich)

been developed from the higher molecular weight polyisobutylenes. The general characteristics of the polymers are toughness and chemical inertness. In order to promote the cross-linkage brought on by vulcanization with sulfur, a few per cent of a diolefin, *e.g.*, isoprene, are copolymerized with isobutylene, thus introducing the necessary points of unsaturation. Some valuable synthetic rubbers have been prepared with such compounds ("Butyl" rubber, for example)<sup>7</sup>. This type of synthetic rubber is chemically inert and well adapted for compounding into automobile tires and inner tubes.

Among the earliest uses proposed for polyisobutylene was its application as the interlayer in automobile safety glass manufacture. Because

of its good adhesive properties and low temperature flexibility, polyisobutylene showed promise in this direction<sup>8</sup>, though the vinyls were preferred commercially. Polyisobutylenes were used in other adhesive fields, for example, in wood veneers, and adhesive plasters; for such adhesives they were prepared at  $-40$  to  $-80^{\circ}$  from pure raw materials<sup>9</sup>. Wood, metals, glass, and concrete were bonded with these high molecular weight polymers<sup>10</sup>. The compatibility with waxes and linseed oil was recognized in the manufacture of adhesive plasters from polyisobutylene<sup>11</sup>.

The advantages of increased adhesiveness imparted to lubricating oils and greases by high molecular weight polyisobutylene are quite marked. Using less than 5 per cent of a polyisobutylene of average molecular weight over 30,000<sup>12</sup> and lubricating oils and greases, blends are produced having improved adhesion to moving metal surfaces because of increased viscosity and stringiness. Solutions of polyisobutylene in certain paraffinic oils are used as additives to the greases. The effect upon the viscosity of oils is shown below:

Type of Oil	Viscosity at 100°—Standard Saybolt Units	
	original	with 5% of 73,000 mol. wt. polyisobutylene
Paraffinic	45.0	1480
Paraffinic	86.5	8050
Naphthenic	47.5	2000

In general the weathering characteristics of asphalts are improved through the addition of small amounts of polyisobutylene. Lower molecular weight portions are particularly compatible with the asphalts.

In further adaptations as adhesives, non-drying varieties were prepared from low molecular weight polyisobutylene of 3000 to 8000 average molecular weight<sup>13</sup>. The other extreme was followed in adhesives for rubber compounds, when molecular weights of 250,000 were mixed with talc<sup>14</sup>. Insulating compounds and floor covering were also prepared with this high molecular weight polyisobutylene.

Abrams and Forcey were among the first to recognize the potentialities of polyisobutylene in the manufacture of pressure-sensitive tapes<sup>15</sup>, which may be applied to a great variety of surfaces simply by pressure of the fingers and which can readily be removed without leaving any 'mark-off' or adhesive deposits. Polyisobutylene, as well as ethylcellulose, natural rubber, synthetic rubber and rubber derivatives were indicated as cohesive agents. To these may be added adhesive agents which impart tack or adhesion to other surfaces. Control of the adhesive agent is possible through plasticizers which must dissolve both the cohesive agent and ad-

hesive agent. Application as hot melts was made possible by various formulations. Adhesive compositions are described in the following manner<sup>15</sup>:

Cohesive Agents 15-60%	Adhesive Agents 10-50%	Plasticizer 5-45%	Modifier 4-45%
Polyisobutylene	Ester gum	Methyl abietate	Hydrogenated
Ethylcellulose	Hydrogenated	Soft alkyds	waxes
Natural and Syn- thetic Rubbers	Rosin	Soft cumars	Vegetable and ani- mal waxes
	Hard Cumars	Dibutyl phthalate	Mineral waxes
	Alkyds	Diethyl phthalate	
	Pitch	Chlorinated Di- phenyl	
	Rosin	Tricresyl phos- phate	
	Toluene-sulfon- amide-formalde- hyde		

While not very specific the above description does, however, suggest a wide variety of materials for adhesive compositions. A permanently adhesive tape using polyisobutylene of 2000 to 70,000 molecular weight was prepared without extensive use of modifying agents<sup>16</sup>. Cold flow in polyisobutylene was reduced through copolymerization with vinyl carbazole<sup>17</sup>. Decided advantages were also observed by combining polyisobutylene and graphite as an adhesive material<sup>18</sup>. Copolymerized with diethyl and diallyl fumarates, polyisobutylene yielded clear solids which showed promise for coatings as well as adhesives<sup>19</sup>.

Thron proposed a mixture of paraffin wax, polyisobutylene and polybutylenes, and polyvinyl ethyl ethers as a water repellant material and adhesive<sup>20</sup>. Chlorinated polyisobutylene (50 per cent chlorine content) and chlorinated paraffin wax (30 per cent chlorine content), when dissolved in carbon tetrachloride serve as coating for concrete<sup>21</sup>. Plasticization of the chlorinated polyisobutylene is necessary because the product becomes more brittle as more chlorine is chemically combined. When rubber stocks became depleted after the start of the second World War, manufacturers of pressure sensitive adhesive tapes turned to other raw materials. Polyisobutylene in particular was prominently featured as a replacement for rubber adhesives. One flexible sheet or tape was prepared with polyisobutylene plasticized with wood rosin as a tack producer to render it pressure sensitive<sup>22</sup>.

Tierney developed general purpose adhesives for pressure sensitive coatings on paper, leather, glass, rubber, and cellulosic films, characterized by clear, colorless transparency. The primary components of his adhesive compositions were: (1) special type of hydrogenated cumarone-indene

resin used for imparting tackiness, (2) an elastomer base comprising rubbery polyisobutylene with a molecular weight greater than 25,000, and (3) a volatile vehicle in which these components are dispersed<sup>23</sup>. The dark color of the ordinary coumarone-indene resins is sometimes objectionable; it is claimed these resins do not have the tack producing qualities and stability of the hydrogenated varieties<sup>24</sup>, which are lighter in color. The cohesive strength of the polyisobutylene polymer may be improved somewhat by the addition of cyclized rubber (1 part to 3 parts of polyisobutylene). The following are examples of typical adhesive solutions<sup>23</sup>:

*Example 1*

	parts
Polyisobutylene, 52,000 mol. wt.	100
Zinc oxide	50
Hydrogenated coumarone-indene	40
Methyl abietate	20
Butyl stearate	10
Heptane	700

*Example 2*

Polyisobutylene, 115,000 mol. wt.	150
Cyclized rubber ("Pliolite")	50
Liquid paraffin oil	50
Hydrogenated coumarone-indene m. p. 85°	50
Heptane	750

An improvement in the viscosity index and adhesiveness of lubricating oils is possible not only with polyisobutylene, as already pointed out, but even more so by the addition of copolymers of isobutylene and phenyl acetylene. The reaction is carried out at low temperatures in the presence of a Friedel-Crafts reagent consisting of aluminum chloride dissolved in an alkyl halide<sup>25</sup>, to form the copolymer.

Emanuel applied the adhesive qualities of polyisobutylene to the attachment of difficultly soluble polyvinylidene chloride liners<sup>26</sup>. Hydrogenated rosin and terpene polymers were employed as plasticizers. High molecular weight polyisobutylene was introduced as a binder for plate glass in safety glass manufacture<sup>27</sup>. Polyisobutylene was also dissolved in monomeric styrene which was activated with benzoyl peroxide. This can be employed as an adhesive primer for the attachment of polyisobutylene sheets to metal surfaces.

Combinations of polyisobutylene and coumarone-indene resins were milled together to obtain a blend with superior adhesive properties, particularly to metals. A preference was expressed for a polycoumarone-indene resin, in which the indene component was predominant. When a blend of approximately equal amounts of polyindene and polyisobutylene was prepared, the material became quite tacky at 100°. In tensile shear

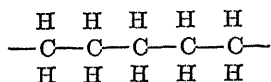
tests upon steel metal strips, considerably greater strengths were realized than with polyindene or polyisobutylene alone<sup>28</sup>.

Hill employed polyisobutylene of 3000 to 20,000 molecular weight as a binder for glass fabrics used as insulation in an electrical generator<sup>29</sup>. Swain discussed the preparation of adhesives and chemically resistant coatings from combinations of polyisobutylene and melamine-formaldehyde, with a molar ratio of polyisobutylene to thermosetting resin of at least three to two. The two resins are generally combined in the presence of xylene and cured with the aid of an acid catalyst<sup>30</sup>. The melamine-formaldehyde resin is prepared in the presence of butanol and concentrated to 60–70 per cent solids by vacuum distillation.

In further research on pressure sensitive adhesives, Mack prepared some types from polyisobutylene, employing a high molecular weight component (over 30,000) and a liquid or semi-liquid polymer (1000 to 7000 mol. wt.) to control adhesive properties. As plasticizers methyl abietate or dihydromethyl abietate were suggested. In addition a small amount (2 to 15 per cent) of a liquid fatty mono ester such as butyl stearate was added as a stabilizer to improve the aging of the adhesive film in sunlight<sup>31</sup>. Polyisobutylene has also been stabilized with 0.01 to 3 per cent of sulfur<sup>32</sup>.

### Polyethylene

Polyethylenes, solid polymers of ethylene gas, are of interest in the adhesives field largely from a fabrication and bonding point of view. The assembly and application of sheets of polyethylenes will become more and more important in developing chemically resistant surfaces and electrical insulation because of the unique resistance offered by the materials. While the polymerization of ethylene to liquids and sticky gums at high temperatures has been known for some time, the production of solid and flexible polymers is more recent. Ethylene gas mixed with traces of oxygen (0.03–0.10 per cent) is polymerized under pressures of 1200 atmospheres and temperatures of 100–300°, to form a polymer of molecular weight above 6000<sup>33</sup>. The polymer has the following structure:



*Polyethylene*

The polymer melts rather sharply between 110 and 120°. It has been applied as insulation for electric wire and cable, used as a moisture-proof sheet, or molded and extruded. It is inherently a flexible polymer which does not readily become brittle at low temperatures, while its low dielectric loss makes it valuable as electric insulation for high frequency material.

Chlorinated derivatives also find some use<sup>34</sup>, though they are a harder variety of plastic.

The resistance offered by polyethylene to most organic solvents, except for heated aromatics, makes the material less desirable from an adhesive standpoint than other types of thermoplastics. The average molecular weight for commercial polyethylene is stated to be 18,000 to 20,000<sup>35</sup>. Tensile strengths of 1800 psi, elongations of 600 per cent, and specific gravity of 0.92 are reported. Polyethylenes may be blended with various waxes. Lower molecular weight oily fractions would be preferred in such combinations.

Child, Clarke, and Habgood developed a technique for bonding polyethylenes to metals, stone, ceramics, etc., by hot-rolling 1 to 2 parts of polyethylene with 1 part of cyclo-rubber<sup>36</sup>. Aside from this special composition the best method of attaching polyethylene to other surfaces appears to be through the medium of hot-spraying of powdered polymer, which is melted in the hot flame and sprayed against the surface. Heat welding operations may also be practiced with success. Good adhesion may be expected from this technique of application, which has been worked out largely with the aid of the Schori spray gun<sup>37</sup>. The polymer appears to be an ideal covering material for concrete and metal surfaces, containing no solvent at all at the time of spraying.

### Coumarone-Indene Resin Adhesives

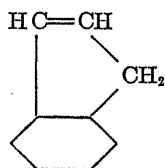
The role of coumarone-indene resin in the manufacture of adhesives appears to be largely as a modifier for other synthetic resins, though there are certain specific applications in which these resins have stood on their own merits as adhesives. They are available commercially in a wide range of softening points, from heavy viscous liquids to brittle solids. Langton lists the principal resin producing substances found in the coal tar naphtha fraction 150–200°:<sup>38</sup>

(1) Styrene and cyclopentadiene	below 160°
(2) Coumarone	168–175°
(3) Indene	176–182°
(4) Methyl coumarone	185–200°
(5) Methyl indene	200–210°
(6) Dimethyl coumarone	215–225°

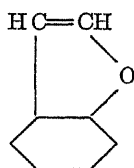
Technical coumarone-indene resins consist principally of mixtures of coumarone and indene polymers, available in colors ranging from pale yellow to dark amber. They are stable, inert resins distinguished by low acidity. In addition they are non-saponifiable, which makes them very attractive as coatings intended to resist alkalis. Kraemer and Spilker

were among the first to prepare coumarone-indene resins by resinifying a crude coal tar naphtha with sulfuric acid<sup>39</sup>. Today the polymerization of coumarone-indene resins is still practiced with sulfuric acid, though the reaction is carefully controlled at temperatures below 20°. Reaction conditions are directed largely toward the production of light colored resins of high melting point<sup>40</sup>. Manufacturers of these resins, however, recommended medium hard grades, with a range of melting points from 110–127°, for adhesive formulations. These resins are described as having a specific gravity of 1.13, a flash point of 270°, refractive index of 1.620, and an average molecular weight of 480 to 700<sup>41</sup>.

The chemical structure of coumarone and indene are shown below:

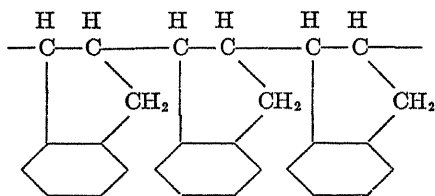


Indene

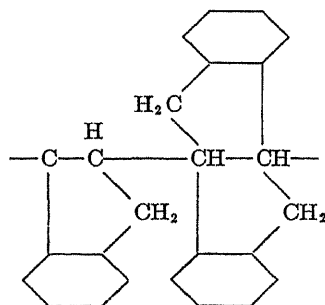


Coumarone

Two alternative structures for the polyindene resin are shown below. Indene tends to polymerize more readily than coumarone, requiring weaker acids as polymerization catalysts.



Polyindene



It is generally necessary to combine the coumarone-indene resin polymers with higher molecular weight organic plastics in order to obtain sufficient cohesive strength to form a good adhesive. The resins possess excellent compatibility with many waxes such as ceresin, japan, and montan wax. Certain grades are only partly compatible with paraffin wax. Solubility in a wide range of substances is characteristic of the coumarone-indene resins, including practically all the usual oils, thinners, and solvents used in the manufacture of surface coatings, with the exception of alcohols. Most esters, ethers, aldehydes, ketones, and chlorinated hydrocarbons are

good solvents. Generally raw and heat bodied oils are better solvents than the blown or oxidized oils. Dehydrated castor oil, but not pure castor oil, is a solvent for coumarone-indene resins. Concerning the compatibility of the coumarone-indene resins with higher polymers, detailed comparisons have been made (see Table 13).<sup>41</sup>

Table 13. Grades of Coumarone-Indene Resins. (Data-Neville Co.)

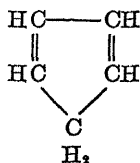
Substance Tested	Hard and Medium Hard m. 110-142°			Soft and Medium Soft m. 5-94.9°		
	Weight Ratio of Cumarone-Indene Resin to Substance under Test					
	9/1	1/1	1/9	9/1	1/1	1/9
Glyceryl-phthalate	P	P	P	P	C	C
Maleic anhydride-cyclo-penta- diene "adduct"	C	C	C	C	C	C
Cellulose Acetate	I	I	I	I	I	I
Cellulose Nitrate	I	I	I	I	I	I
Ethylcellulose	P	P	C	P	P	C
Polystyrene	C	C	C	C	C	C
Polyisobutylene	I	I	I	I	I	P
Chlorinated biphenyl	C	C	C	C	C	C
Phenol-formaldehyde	C	C	C	C	C	C
Polymethyl methacrylate	C	C	C	C	C	C
Polyvinyl butyral	P	P	P	P	P	P
Urea-formaldehyde	P	P	P	P	P	P
Polyvinyl acetate	I	I	I	I	I	I
Shellac	I	I	I	I	I	I
Dammar gum	C	C	C	C	C	C

C = Compatible. P = Partially compatible. I = Incompatible.

In addition to the grades of coumarone-indene noted in table 13, which are of potential interest to the manufacturers of adhesives, are phenol-modified coumarone-indene resins and hydrogenated coumarone-indene resins. The phenol-modified coumarone-indene resins are produced by polymerizing coumarone-indene in the presence of phenols or cresols and activated clay at temperatures of 100°<sup>42</sup> or at lower temperatures in the presence of sulfuric acid<sup>43</sup>. Compatibility with alcohols and polyvinyl acetals to form adhesive compositions is characteristic of the phenol-modified coumarone-indene resins<sup>44</sup>. The hydrogenated coumarone-indene resins and their application to polyisobutylene adhesives have already been described<sup>24,23</sup>. The hydrogenation apparently removes the exposed double bonds in the six-membered rings of the polymer, though Carmody and Tierney describe the hydrogenation of coumarone-indene as taking place in three zones. Hydrogenation of one zone occurs with a nickel catalyst and inhibits the fulvene reaction which causes darkening, while more drastic measures are required for the hydrogenation of the

next zone. Ten per cent catalyst and temperatures of 225° and hydrogen pressures of 1000 psi are employed. "Buried" double bonds are reached in the remaining zone<sup>45</sup>. Water white resins are obtained through the hydrogenation process.

The presence of cyclopentadiene with coumarone-indene resins may have beneficial effects. Carmody, Sheehan, and Kelly described the production of light colored resins from 60 to 65 per cent dicyclopentadiene, 15 to 20 per cent indene, and 5 to 10 per cent coumarone<sup>46</sup>. Dicyclopentadiene may also be obtained commercially, and the monomer formed directly from it (see formula below), or else it is available in the form of a polymer (Neville "G" resin). Cyclopentadiene reacts with maleic anhydrides to form "adducts", already described as useful adhesives.



*Cyclopentadiene*

Ellis has employed solutions of coumarone-indene resin to coat the surface of concrete and render it more waterproof<sup>47</sup> and also to waterproof fabric<sup>48</sup>. In conjunction with shellac, coumarone-indene resins have been used in the manufacture of grinding wheels<sup>49</sup>. Shaffer also tried a solution of coumarone-indene resin, rubber cement, and a paraffin wax in gasoline solvent as a water-proofing material for fabrics<sup>50</sup>. McCoy prepared a cement by heating a mixture of 10 to 50 per cent gutta percha, 50 to 80 per cent coumarone-indene resin, and a filler such as precipitated chalk, at an elevated temperature<sup>51</sup>.

Mixed coumarone-indene resins and Portland cement have been proposed as strongly adhering surfacing agents for floors or roads. These have been dispersed in rubber latex<sup>52</sup>. Allen employed coumarone resins and portland cement as a binder or adhesive for linoleum<sup>53</sup>, while Daimler and Thron prepared a linoleum adhesive by mixing coumarone resins in a mixture of isopropyl alcohol and benzene<sup>54</sup>. Coumarone resin dissolved in a nitroparaffin solvent shows good adhesion for bituminous surfaces<sup>54a</sup>.

Adhesive compositions combining rubber and coumarone-indene resins are well known. An adhesive has been prepared for example, from 2-5 parts of Karaya gum, 25 parts of coumarone-indene, 17 parts of machine oil, and 100 parts of a rubber latex (33 per cent solids)<sup>55</sup>. Blumberg prepared an adhesive composition by kneading together at 140° 100 parts of coumarone resin and 15 parts or less of vulcanized rubber<sup>56</sup>.

Chlorinated rubber and rubber hydrochloride when employed in con-

junction with coumarone-indene resins form useful adhesive products. Winkelman described several products containing rubber hydrochloride, chlorinated paraffin wax, and a soft paracoumarone-indene resin. Other products he mentioned contained ester gum; in another, sulfur was used with the rubber hydrochloride and coumarone resin<sup>57</sup>. Kenney found a useful crack and woodwork filler prepared with 2 to 5 parts of paracoumarone resin, 1 to 4 parts of chlorinated rubber, 3 to 15 parts of toluene, and wood flour added to a doughy consistency<sup>58</sup>. Kerr prepared a number of pressure sensitive adhesive tapes with a paracoumarone resin which softened at 50°. To 5 to 10 parts of the coumarone resin he added 1 part of chlorinated rubber (65-70 per cent chlorine content) and produced a solution by heating at 150°. This adhesive was employed without any solvents and was hot melted to the cloth backing<sup>59</sup>.

Mastic floor tile compositions have successfully employed coumarone-indene resins in their binders. A hard, pale resin is ordinarily selected and blended with oils, pitches, and plasticizers to obtain a light colored binder. Asbestos and various pigments are generally added and various mottled colors are developed. Bonney and Maguire employed polymerized tung oil (1 part) to 3 parts of coumarone-indene resin as the binder in their composition<sup>60</sup>, while Schlaanstone worked with some rosin derivatives<sup>61</sup>. In the latter composition the binding agent consisted of asphalt and coumarone-indene resins, 60 to 95 per cent plasticizer from gelled drying oils, and 5 to 40 per cent liquid rosin esters and hydrogenated rosin esters to improve wetting power of the plasticizer for the fibers. Dimers of coumarone-indene resins, light oily type plasticizers, have also been employed in mastic floor tile manufacture<sup>62</sup>.

Chlorinated diphenyls are frequently mentioned as a plasticizer in coumarone-indene resin adhesives. In one example, an adhesive was made up of 25 per cent viscous chlorinated diphenyl, 50 per cent solid chlorinated diphenyl, and 25 per cent coumarone-indene resin.<sup>63</sup>

Coumarone-indene resins deposited from a xylene solution upon a flash coating of copper on zinc or tinned steel wire are claimed to improve greatly the adhesion of the rubber to the metal after vulcanization. This process was applied particularly to the preparation of ferrous tire beading wires<sup>64</sup>.

Coumarone-indene resins have been the subject of much investigation in developing hot melt or solvent type adhesives. Hot melts offer much promise because of the thermoplasticity of the resins and the ease of melting them. A nonsolvent adhesive coating has been prepared from 3 parts of a hydrogenated coumarone indene resin and 1 part of a linear polybutene<sup>64a</sup>. Good water resistance is also possessed by the adhesives formulated with major components of these resins. One of the manufacturers of these resins recommends the following as a linoleum cement<sup>41</sup>:

283 Coumarone-indene resin	
140 parts of benzene	
71 parts of denatured alcohol	
412 parts of whiting	
55 parts of 2.75 parts of pale crepe rubber in 53 parts of benzene	

All ingredients are churned together with the exception of the whiting which is ball-milled in with the other ingredients to give a uniform dispersion. There have been specially developed water dispersible resins prepared from the coumarone-indene resins which will blend quite readily with rubber latex to yield a useful adhesive.

Phenol modified coumarone-indene resins discussed in the preceding pages offer promising results in preparing adhesives largely because they act as solubilizing agents between synthetic resins and other coumarone-resins. For example, the following represents a typical hot melt adhesive:

Phenol modified coumarone-indene	parts
	20.0
Medium soft coumarone-indene	66.7
Polyvinyl acetate (AYAF)	8.3

The melt is best prepared in an inert atmosphere, the phenol modified coumarone-indene resin being melted at 150–170°, after which the polyvinyl acetate is added. When the melt clears the coumarone-indene resin may be introduced. A chart showing the compatibility of these three components appears in Figure 24<sup>41</sup>.

Zeeh recently reviewed the usefulness of coumarone-indene resins as extenders for rubbers and plastics. He also brought out that as little as 1 to 2 per cent of diatomaceous earth filler will impart high molten viscosity to the resins, and hence may be useful in controlling hot melt applications<sup>65</sup>.

In addition to the coumarone-indenes, some use has been made of the polycyclopentadienes as adhesives. Soday discusses a few applications of hydrogenated polycyclopentadiene in combination with crepe rubber to form adhesives<sup>66</sup>. The hydrogenation was carried out at high pressures of 350 to 1500 psi and temperatures of 25 to 100° in the presence of a platinum catalyst. Soday also discusses the technique of hydrogenating polycyclopentadiene in addition to describing coating and adhesive applications.

### Polyamides as Adhesives

Polyamides have attracted considerable attention as a synthetic fiber forming material used in the manufacture of textile products, various brush bristles, and molded products. Bolton traced some of the early history and the background leading to the development of the polyamides<sup>67</sup>. He pointed out that many of the developments in super polyesters were

initiated by Carothers, who first prepared on February 28, 1935, a polymer of hexamethylenediamine and adipic acid, which was selected for initial manufacture. Generally speaking the polyamides are made from the condensation products of dibasic acids and diamines, and numerous

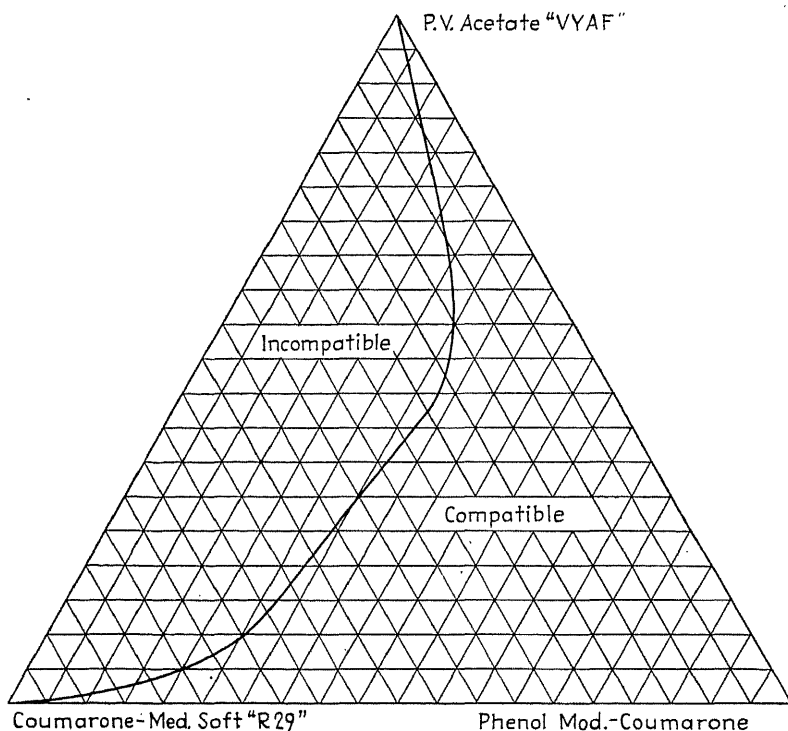
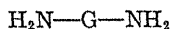
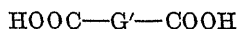


Figure 24. Range of compatibility of polyvinyl acetate, coumarone-indene resin, and phenol-modified coumarone resin.

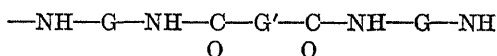
combinations are possible to yield materials with widely varying properties. The general reaction formula is:



*Diamine*



*Dicarboxylic Acid*



*Polyamide*

As examples, some of the diamines and dicarboxylic acids which were considered early in the manufacture of the polyamides were the following typical compounds<sup>68</sup>:

<i>Dibasic Acids</i>		<i>Diamines</i>	
Oxalic acid	HOOC COOH	Ethylene diamine	$\text{NH}_2 \cdot (\text{CH}_2)_2 \text{NH}_2$
Malonic acid	$\text{HOOC}(\text{CH}_2)\text{COOH}$	Tetramethylene diamine	$\text{NH}_2(\text{CH}_2)_4\text{NH}_2$
Succinic acid	$\text{HOOC}(\text{CH}_2)_2\text{COOH}$	Pentamethylene diamine	$\text{NH}_2(\text{CH}_2)_5\text{NH}_2$
Adipic acid	$\text{HOOC}(\text{CH}_2)_4\text{COOH}$	Octamethylene diamine	$\text{NH}_2(\text{CH}_2)_8\text{NH}_2$
Pimelic acid	$\text{HOOC}(\text{CH}_2)_6\text{COOH}$	Hexamethylene diamine	$\text{NH}_2(\text{CH}_2)_6\text{NH}_2$
Suberic acid	$\text{HOOC}(\text{CH}_2)_8\text{COOH}$	Decamethylene diamine	$\text{NH}_2(\text{CH}_2)_{10}\text{NH}_2$

The early polyamide resins possessed high melting points, insolubility in most solvents, and the ability to be cold drawn into resilient fibers. They were also cast into thin sheets from a solution of formic acid with a trace of hydrochloric acid. Typical polyamides were polyhexamethylene adipamide (m.  $248^\circ$ ), polydecamethylene adipamide (m.  $230^\circ$ ) and poly-pentamethylene sebacamide (m.  $195^\circ$ ). In general, the method of preparing the polyamide requires first the reaction to form the polyamide salt from the diamine and dicarboxylic acid in solution. The solution is concentrated and then polymerized in an autoclave. Molecular weights of greater than 10,000 are necessary to form the fibers. The polyamide is then chilled on the surface of a rotating wheel to harden. After chipping into flakes it is purged of oxygen with nitrogen, melted down, filtered, and forced through spinnerets under pressure<sup>69</sup>.

In the synthesis of two of the most important raw materials, adipic acid and hexamethylene diamine, phenol may serve as the starting point. Phenol is converted to cyclohexanol, which is reacted with nitric acid to form adipic acid. Adipic acid is reacted with ammonia to form adipic diamide, which is dehydrated to adiponitrile. The latter compound is hydrogenated to hexamethylene diamine.

The many possibilities of the polyamide resins may be appreciated from the wide variety of properties which may be incorporated into the final compounds. Copolymers and the addition of small amounts of unsaturated dicarboxylic acids will help to promote cross-linkage. From the adhesives point of view, the high melting point types which are soluble with difficulty in phenol, *meta*-cresol, resorcinol, and formic acid do not appear to offer as much potential interest as some of the lower melting point heat convertible types. Of course, hot melts of the former have exhibited promise as adhesives, though temperatures are somewhat high. Considerable work has been done to improve the solubility of the polyamide type of resins and a number have been obtained by reacting polymethylene diamines with maleic acid<sup>70</sup>. These resins are softer than the other fiber forming types. For example, fumaric acid plus decamethylene diamine forms a resin with a melting point of  $45$  to  $50^\circ$ , and muconic acid plus ethylene diamine forms a resin with a melting point of  $61^\circ$ . Because of the unsaturation introduced by the dicarboxylic acid selected, thermosetting properties valuable to molding and to hot setting adhesives appear.

These resins are soluble in alcohols, glycols, and benzene in some instances. A water-soluble polyamide is prepared by condensing 75 parts of hexamethylenediamine adipate with 23 parts of  $\alpha$ -amino caproic acid hydrochloride at 211 to 222° in the absence of air<sup>71</sup>. Hagedorn has also prepared a hydrophilic synthetic linear polyamide <sup>71a</sup>.

Another technique of modifying the properties of the polyamides in order to get good solubility in organic solvents is to employ amino or acid components with oxygen or sulfur in the hydrocarbon chain<sup>72</sup>. A few examples include:

Fiber Forming Materials	Soluble In	M.P. (C°)
Triglycol diamine-adipic acid	Water, alcohol, dioxane	185°
Hexamethylene diamine-diglycollic acid	Alcohol, diethylene glycol	145°
Decamethylene diamine- <i>p</i> -diphenylolpropane diacetic acid	Ether	65°

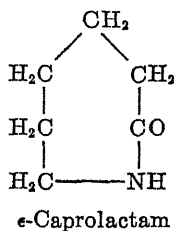
The last mentioned type is compatible with nitrocellulose and drying oil modified alkyds. These particular examples illustrate polyamides of potential value to the field of adhesives. Carothers also describes safety glass applications of these polyamides<sup>72</sup>, and other readily soluble polyamides useful for coatings, packaging materials, and adhesives. Ethylene diamines are reacted with fatty acids from soybean to form polyamides soluble in inexpensive solvents. They exhibit excellent adhesion to glassine paper, sulfite paper, lead foil, cellophane, etc.<sup>73</sup>. They have shown commercial value in application to food containers<sup>74</sup>. Considerable promise is shown as a hot melt or stripping compound. They are compatible in all proportions with low viscosity nitrocellulose<sup>74a</sup>.

Carothers described a number of polyamides compatible with cellulose derivatives and with drying oils, which show promise as coatings, impregnants, adhesives, and sizing materials<sup>75</sup>. Triggs<sup>76</sup> and Graves<sup>77</sup> also described a number of polyamide adhesive products. Stasny discusses the modification of the polyamide resin with dihydroxy sulfobenzidine to obtain useful adhesive products<sup>78</sup>.

Foster developed a technique for preparing thin polyamide films from hexamethylene diamine and adipic acid by extruding the resin upon a slowly revolving drum and carefully controlling cooling<sup>79</sup>. Uses described for these polyamide films are as safety glass interlayers, thin membranes, and coatings. Carothers describes other polyamides formed as thin films, particularly for photographic purposes; he mentions in particular the good adhesion of the polyamides to cellulose nitrate<sup>80</sup>. Austin developed a cork composition employing a fusible linear polyamide as a binder<sup>81</sup>.

Schupp prepared adhesive solutions of polyhexamethylene adipamide, dissolved in a 25 per cent solution of anhydrous calcium chloride in methanol<sup>82</sup>. There is a very limited range in which stable solutions are formed (10 to 30 per cent calcium chloride). These polyamide solutions have been proposed as adhesives for shoes, boxes, cloth, leather, wood, and glass. The alcohol-salt solution is also effective in bonding the polyamide alone.

There was considerable activity in the development of polyamides in Germany during the war, and their efforts leaned toward the production of softer types, more easily dissolved. A number of formulations appeared with resins prepared from caprolactam, which is illustrated below:



Caprolactam is capable of self polymerization by opening of the ring to form a linear polymer, of the same structure as shown previously for a polyamide. Polymerization is carried out at elevated temperatures. There are several methods available for synthesizing caprolactam. One of the starting points is cyclohexanone, which is reacted with hydroxylamine and then converted to a seven member ring. The other starting material can be tetrahydrofuran, which after reaction with carbon monoxide, is carried through several stages to the caprolactam<sup>83</sup>.

As indication of the growing trend in using coatings and adhesive substances involving caprolactam, is a composition involving 40 parts of hexamethylenediammonium adipate; 30 parts of hexamethylenediammonium sebacate; and 30 parts of caprolactam<sup>84</sup>.

Solvents for the solid polyamides used in this country for molding compounds and synthetic fibers are relatively few and unsuited to solvent welding of the material. Hot formic, phenol, and resorcinol will dissolve 'nylon', though would be unsuited as cements. Resorcinol-formaldehyde resins and furane resin polymers will however bond very satisfactorily to 'nylon'. The adhesion of 'nylon' yarn to rubber has been improved by pre-treatment with phenol or resorcinol<sup>85</sup>. Laminated polyamide foils have been prepared with an adhesive layer of amino caproic acid (35-70%), hexamethylene diamine, and adipic acid<sup>86</sup>.

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## Chapter 8

### Rubber Adhesives

Natural and synthetic rubbers and their derivatives have been utilized in the preparation of many adhesive substances. The development of rubber adhesives precedes by a number of years the efforts made with synthetic resins, though today both groups are the subject of active attention in the adhesives field. It is desirable to examine rubber adhesives at this point because so many of their formulations are made in conjunction with synthetic resins. Their applications vary from the pressure-sensitive tapes to the bonding of sheet aluminum alloy. With high initial tack and good flexibility, rubber-base adhesives are widely accepted in innumerable applications.

While natural rubber sources were the focal point of attention up to the start of World War II, increasing attention has been given in recent years to the development of adhesives from the synthetic rubbers such as butadiene-styrene copolymers or the butadiene acrylonitrile copolymers. Each material has its own peculiar problems; but an attempt will be made to review the status of the art of rubber adhesives, particularly those aspects which may help our understanding of the theories of adhesion, as well as those features which run parallel to the work on the synthetic resins.

Rubber-like materials possess peculiar advantages over the more rigid synthetic resins as adhesives. Not only are they capable of developing good specific adhesion for various surfaces, but when an effort is made to rupture this bond, their high elongation permits the adhesive film to absorb much of the strain. On the other hand, a more brittle resin adhesive tends to develop greater stress concentrations at the time of loading. Notwithstanding, developments of adhesives from natural and synthetic rubbers are not necessarily confined to stretchable adhesive films, because some of the best properties have been exhibited by rubber derivatives distinguished by high specific adhesion for metal surfaces rather than their elasticity.

The industrial utilization of rubber paved the way for general acceptance of rubber adhesives. It has been pointed out, for example, that Macintosh obtained a patent in 1823 for rendering two fabrics waterproof by uniting them with a solution of rubber<sup>1</sup>. Early patents on rubber adhesives specified rubber solutions<sup>2</sup> and their applications directed to coating

and adhesive problems. As will be brought out in the text to follow, there are many factors which will influence the adhesive action of rubber or rubber-like compounds.

It will prove desirable to establish a few classifications for rubber adhesives before undertaking an analysis of rubber cements. These may be grouped in the following manner:

#### Types of Rubber Adhesives.

1. Natural rubber latex (major component)
2. Solution of rubber in suitable solvent
3. Cyclized rubbers:
  - (a) By sulfuric or sulfonic acids ("Thermoprene", "Vulcalock")
  - (b) By chlorostannic acid ("Plioform" and "Pliolite")
4. Phenol-modified rubbers (Phenol or beta-naphthol ("Isolac"))
5. Oxidized rubbers ("Rubbone")
6. Chlorinated rubbers in solution ("Parlon" and "Ty-ply")
7. Rubber hydrochloride ("Pliofilm" and "Marbon" V and X)
8. Solutions of chloroprene (neoprene cements)
9. Olefine polysulfide cements ("Thiokol")
10. Miscellaneous synthetic rubber cements
11. Chlorinated and cyclized synthetic rubber cements

#### ADHESIVES FORMULATED WITH RUBBER LATEX

The properties of rubber latex are substantially those of a finely dispersed colloid, with particle size ranging from 0.5 to 3 microns in diameter; they are negatively charged, are in a constant state of Brownian movement, and are highly susceptible to the addition of small amounts of other agents. The amount of rubber actually present in latex varies, averaging around 38 per cent. After it has been tapped from the tree a small amount of preservative, 0.5 to 1 per cent of ammonia, is generally added to counteract acid-forming bacteria. Natural rubber latex shows properties which are both lyophilic and lyophobic<sup>3</sup>. The hydrocarbon system which is rubber,  $(C_5H_8)_x$ , is lyophobic, though surrounded by a lyophilic protein which has some affinity for the water in which it is dispersed. The relationship between viscosity and concentration is shown in Figure 25, obtained from data by Murphy<sup>4</sup>, demonstrating the rapid increase in viscosity after a certain solids content is reached.

The viscosity characteristics of rubber latex are greatly dependent upon certain addition agents, particularly colloidal clays (such as bentonite) which form thixotropic dispersions in water<sup>5</sup>. These clays are frequently mentioned in the preparation of adhesive formulations involving rubber latex.

As compared to true solutions of rubber as rubber cements, the latex adhesives have the drawback of being slower drying, due to the presence of

slowly evaporating water, and in not having the tackiness of the solvent types. Nevertheless, rubber latex has much higher solids content and lower viscosity than solvent-type cementing agents. Besides, there are no toxic solvents to be added. Van Nederveen, in reporting on the impregnation of cotton yarns with rubber latex, determined a number of factors influencing the effectiveness of the penetration into the fiber<sup>6</sup>. He pointed out that rubber solvents deposit a superficial coating of adhesive on the surface of the fibers, while under proper conditions latex will penetrate much better and secure better mechanical bonds to the fibers. He recommended treatment of the cotton fibers with a wetting agent be-

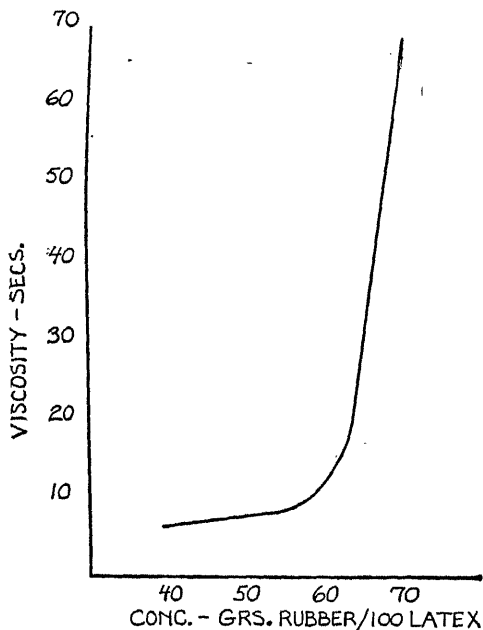


Figure 25. Relationship between viscosity and concentration for rubber latex

fore application of the rubber latex, and examination of photomicrographic data, rather than determination of the weight absorbed, to indicate the efficacy of this technique. Quaternary ammonium compounds have worked out satisfactorily as wetting agents for rubber to fabric bonds<sup>6a</sup>.

Lejeune and Bongrand achieved thorough distribution of the latex into the cotton fibers by treating the fibers with latex before they were twisted into yarn<sup>7</sup>. Ditmar pointed out the advantages of rubber latex adhesives for wood, cloth, paper, glass, and metal application<sup>8</sup>. The desirability of adding some preservative or protective colloid to stabilize the latex adhesive has long been recognized. Schidrowitz added solutions of glue,

gelatin, casein, or starch to rubber latex and prepared a number of useful adhesive formulations<sup>9</sup>.

The combination of rubber latex and rubber cements to develop superior adhesives were first proposed by Ditmar<sup>10</sup>, and a number of useful combinations along these lines were recorded in the years to follow. Many of the applications for rubber latex were conceived by Hancock and Silver, almost one hundred years ago, though industrial utilization of latex directly was more slow to follow<sup>11</sup>. Biddle prepared a large number of latex adhesives, largely employing rubber latex and blood albumen. Among combinations he proposed were: Rubber latex, blood albumen, and para-formaldehyde as an insolubilizer for albumen; rubber, albumen, and a water-soluble silicate; rubber latex, blood albumen, and alkaline-earth hydroxide; and rubber latex, casein, calcium hydroxide, and sodium phosphate<sup>12</sup>.

Rubber latex with additives has been employed in cementing shoe parts together. On evaporation or diffusion of the water into the porous body, a tacky, fine film of rubber is formed, though it may prove desirable to wait until the surfaces are dry before pressing them together<sup>13</sup>. The adhesion of rubber latex has been improved by the addition of chromates or dichromates to the aqueous dispersion<sup>14</sup>. Davis deposited thin rubber latex films over films prepared from rubber solvent cements, in order to secure best bonding qualities<sup>15</sup>.

Holmberg prepared an improved rubber latex adhesive by creaming the latex, adding rosin oil, carbon tetrachloride in emulsion and a deodorant<sup>16</sup>. As adhesive films for cellophane and other materials in tape form, rubber latex has been useful. An aqueous dispersion of rubber (45 per cent) containing 3 to 50 parts, a water-soluble agglutinant (25 to 100 parts) and glycerol (1 to 17 parts) are employed<sup>17</sup>. Bloomfield and Farmer improved the adhesive properties of latex by prolonged heating with hydrogen peroxide<sup>18</sup>. The final product was preserved with ammonia, and stronger and more uniform bonds were reported between various surfaces. It is probable that the oxidation of the rubber and subsequent depolymerization contributed to the better adhesion.

Dunham used dried milk and an amide as a dispersing agent in which the latex was incorporated to form an adhesive<sup>19</sup>; this was applied to regenerated cellulose. Levin prepared a latex-type adhesive with 2 lbs of latex, 8 lbs of blood albumen, and 15 lbs of water<sup>20</sup>. Goodenow improved the tackiness of rubber latex by including finely divided fossil gum dispersed in the latex<sup>21</sup>. Owen prepared a rubber latex adhesive with dispersed factice<sup>22</sup>. Rubber latex formulations for shoe cements were devised by Teague, a typical composition containing<sup>23</sup>:

100 parts rubber latex (33% solids)  
20 parts ammonium resinate  
280 parts water (in addition to latex)  
24 parts litharge (thickener and accelerator)  
4.2 parts sulfur

Crockett converted latex to a rubber cement by agitating it and slowly adding a solvent such as gasoline. The proportions were one liter of gasoline to 200 cc of 30 per cent rubber latex<sup>24</sup>. He also brought out the fact that better adhesion could be obtained in the rubber compositions with a pH value lower than 7.0. McIver compounded spray-dried formaldehyde-treated rubber latex on a rubber mill, adding rosin and a soap. The compound was then redispersed as a rubber latex and used as an adhesive<sup>25</sup>. Healy prepared a latex adhesive, using vulcanized rubber latex, casein or albumen as a protective colloid, and free ammonia<sup>26</sup>. Wedger added an ammoniacal solution of casein to ammonia-preserved latex. To this was added formaldehyde which reacted with the casein to form a precipitate on the surface of rubber. The pH was adjusted to 8.0 to 8.5 and the solution employed as an adhesive<sup>27</sup>.

Tefft found that a water-soluble cellulose ether such as methylcellulose was useful for creaming rubber latex. He employed 1/2 part of methylcellulose per 100 parts of latex solids<sup>28</sup>. Rubber latex adhesives modified with alkali silicate solutions were prepared by Kliefoth. A solution of sodium fluosilicate was also added to aid the dispersion of the rubber<sup>29</sup>. Reiner reviewed the applications of rubber latex outside of the rubber industry, and pointed out that its principal use was in the leather industry as an adhesive. Adhesive applications for casein plastics were also described<sup>30</sup>. Fuller prepared rubber latex adhesives from the following combinations<sup>31</sup>:

Rubber latex (40-75% solids)	60%
Glycerin	15-40%
Casein	3-8%
Water	20%

McDonald employed rubber latex adhesives in an effective manner. After application of the latex to the surface to be bonded, such as in securing leather or rubber soles to shoe bottoms, the rubber was treated or activated with a solvent or softener before bonding<sup>32</sup>. Adhesives for self-sealing envelopes were prepared with rubber latex (40 to 60 per cent solids) and powdered mica as the sole constituents<sup>33</sup>. Among other efforts to convert the rubber latex to a rubber solvent cement was the technique of adding a rubber solvent such as naphtha, carbon tetrachloride or benzene to rubber latex without coagulation or phase reversal. To this was slowly

added an alcohol such as methyl alcohol until the required viscosity was attained<sup>34</sup>.

Twiss and Neale prepared a permanently tacky adhesive with the aid of rubber latex. To an emulsion of a permanently soft thermoplastic material in water was added ammonium hydroxide. This was followed by 10 per cent rubber latex accompanied by heating<sup>35</sup>. Metcalf employed the same technique in preparing an adhesive for laminating paper. To an aqueous emulsion of pitch or bitumen was incorporated 35 to 70 per cent rubber latex, the rubber solids comprising some 10 to 25 per cent of the total. The net effect was to increase the adhesiveness of the pitch and reduce its sensitivity to temperature. The adhesive deposited on the face of the sheet without excessive penetration and the sheets were pressed together<sup>36</sup>.

Rasmussen employed rubber latex adhesives for bookbinding and tabbing purposes. He cited examples of telephone directory applications. Aqueous rubber latex, protected with a solution or suspension of casein was claimed to be somewhat unstable, the materials tending to settle. The ultimate proportions of casein, latex, and water were so adjusted that the critical ratio of water to casein is below that causing breakdown of the casein solution. He also used a concentrated latex solution, and water (not including that in latex) not to exceed twice the weight of the casein<sup>37</sup>. A typical composition included:

Casein	13%
Centrifuged 72% solids latex	33%
Natural latex (60% solids)	26%
Water	26%
Sodium 2,4,5-trichlorophenate (emulsifier)	2.0%
Ammonium chloride	0.3%

Another formula<sup>1</sup> for tabbing and bottle labels included rubber latex rosin, starch and mineral oil<sup>37a</sup>.

Water-dispersed rubber adhesives were prepared by Livermore from reclaimed rubber, hard asphalt, rosin, and potassium hydroxide. The solids were mixed with sufficient water for inversion to the oil-in-water type of emulsion. Wood rosin provided the resin acids for forming the scap. This adhesive was employed in cementing roof pads on automobile metal surfaces<sup>38</sup>. Further details were also given on the rubber-asphalt dispersions<sup>39</sup>. Spraragen prepared a latex adhesive with up to 25 per cent of a lower alkyl ester of crotonic acid (less than 4 carbon atoms in the alkyl group)<sup>40</sup>. Wening developed a non-slipping adhesive from a rubber latex (9.5 to 11 parts), a tack producer such as ester gum (7.5 to 11.5 parts) and 0.75 to 1.5 parts of a peptizing agent to inhibit coagulation<sup>41</sup>.

Corbin and Britt developed latex adhesives for non-porous surfaces by

modifying the rubber latex with sodium silicate solutions. The adhesives were capable of setting without heat and employed unvulcanized latex with 1 part of 60 to 70 per cent rubber, 2 parts of vulcanized latex (60 per cent rubber), and a sodium silicate composition<sup>42</sup>. The optimum proportions of sodium silicate solution were between 20 and 30 per cent of the total combination. Corbin and Britt established a relationship between the strength of the bond and the proportion of sodium silicate. In other developments of sodium silicates and rubber latex adhesives, the surfaces being bonded were first primed by sodium silicate<sup>43</sup>.

Pinene resin emulsions are capable of combining with various proportions of rubber latex to form useful adhesive products, according to Geiger<sup>44</sup>. Harris developed an adhesive composition with a major proportion of bentonite. He employed 60 per cent of bentonite, 25 per cent of rubber latex, 10 per cent of magnesium chloride, 4 per cent of soap, and 1 per cent of a preservative<sup>45</sup>. Dewey also employed small quantities of rubber in connection with colloidal clay in suspension as adhesives for labels on cans<sup>46</sup>. McGavack and Nikitin prepared latex adhesives from three components: concentrated acidified latex, creamed latex, and acidified latex, and added casein, glue, corn gluten, or egg albumen in addition to vulcanizing ingredients<sup>47</sup>.

Glancy found that the addition of imides of an acid from succinic acid, phthalic, or sulfo-benzoic acid to rubber latex improved the adhesive properties<sup>48</sup>. Metarylenediamine, such as *m*-phenyldiamine reacted with an aldehyde, has been employed as an addition product to rubber latex adhesives<sup>49</sup>. The reaction product of sodium or potassium hydroxide upon sugar has also been reported as a useful additive<sup>50</sup>. Purdon discovered an adhesive for waxed paper comprising 100 parts of rubber latex and 15 to 35 parts of corn syrup<sup>51</sup>.

An increase of the solids content of rubber latex adhesive often appears desirable in the formulation of rubber latex adhesives. In general this is accomplished by one of three methods: creaming, centrifuging, or evaporating. In creaming, the latex is treated with chemical agents such as ammonium alginate, gelatine, glue, gum arabic, and others to accelerate the tendency of the rubber particles to rise. The concentrated fraction is separated. Traube is usually credited with introducing creamed rubber latex for commercial purposes<sup>52</sup>. By centrifuging natural rubber latex a concentration of 60 to 62 per cent solids may usually be obtained, while by evaporating even higher solids content is possible. It has been found possible to cream latex by high frequency heating methods. Stabilizers such as potassium hydroxide are added before this operation, which must be conducted quite slowly in order to avoid forming a skin. The formation of the skin on a rubber latex film presents two problems, which are also signifi-

cant to the adhesive application. The skin forms a film which retards the evaporation of volatiles under it and presents added difficulties in that the rubber polymers in the skin can not readily be dispersed again.

The choice of whether or not to vulcanize rubber latex adhesives will depend on the application of the adhesive. While the latex films may subsequently chemically treated to vulcanize the rubber by hot or cold methods, it is generally much more expedient to compound the latex with the necessary vulcanizing ingredients. The advantages of vulcanization are many, and ever since Goodyear and Hayward discovered the beneficial effects of sulfur upon the strength and durability of rubber goods, reliable applications of rubber products have been assured. In the addition of vulcanizing agents to rubber latex (such as finely divided sulfur, zinc oxide, and one or more organic accelerators), the ingredients must be reduced to a very fine colloidal form so as to be miscible with the latex. Further, to avoid disturbing the water-solids balance, the fillers are preferably wetted beforehand. The dispersion is aided by various wetting agents such as sulphonated fatty acids, soaps, and alcohols. Protective colloids such as a solution of casein in ammonia prevent coagulation of the latex. However, inert fillers do not have the same strengthening effect as they do in crude rubber. The superiority of latex-formed films in strength and durability over processed rubber and its films is generally recognized. Barron brings out this comparison very effectively<sup>5</sup>.

The latex treated with vulcanizing ingredients may be expected to give greater shear strength, less creep under stress, and more durability as an adhesive than pure unvulcanized latex adhesive. However, the presence of these vulcanizing ingredients tends to make the adhesive solution less stable and the shelf life much shorter. The adhesive latex mixtures so prepared may be classified as either heat-vulcanizable, self-vulcanizable (capable of curing at room temperature), or pre-vulcanized. In the latter example, discovered by Schidrowitz, the rubber globules are vulcanized while still in dispersion<sup>53</sup>. A typical general purpose latex mix which will vulcanize in 10 minutes at 110° contains:

Rubber (as 60% latex)	100
Zinc oxide	1
Zinc dimethyldithiocarbonate	1
Mercaptobenzthiazole	0.2
Sulfur	1
Casein (10% solution)	1

#### SOLVENT TYPE OF RUBBER CEMENT

The most important solvents for rubber are derived largely from petroleum and coal-tar fractions, solvent naphtha and benzene being most

widely used. Others, such as gasoline, carbon disulfide, carbon tetrachloride, and trichloroethylene are also used in large quantities. The ease with which rubber enters solution depends a good deal upon its previous history, though the action generally takes place in two stages, swelling followed by a true solution. Highly viscous solutions are formed which are capable of depositing tacky, adhesive films.

Many of the early patents on rubber cements dealt largely with the solutions of rubber in different solvents. Rossman reviewed many of the early patents taken out in the United States dealing with some rubber cements, describing some 105 references on them up to 1935<sup>54</sup>. Among some of the earlier patents of note was the rubber cement prepared by Jeffery, who dissolved one pound of shredded rubber in 4 gallons of naphtha. On heating this combination small amounts of shellac were introduced.<sup>55</sup> Hayward described the technique of bonding rubber to rubber with the aid of a rubber cement, followed by vulcanization<sup>56</sup>. Grout prepared useful cements from unvulcanized rubber, benzene, turpentine, and collodion<sup>57</sup>. Kelly indicated the trend of the art toward vulcanizable compositions by adding sulfur, sodium silicate, and white lead to the rubber<sup>58</sup>.

In order to compare the viscosities of rubber solutions with other solutions of synthetic resins described in preceding chapters, some of the work of Madge is indicated in the following table<sup>59</sup>:

Comparative Viscosities of Rubber Solutions and Latex.

	Concentration	°C	Viscosity (cps)
Rubber solution (in benzene)	10 gm per 100 cc	20.0	342
	20 gm per 100 cc	21.7	7730
	25 gm per 100 cc	18.5	26950
Natural rubber latex	38 gm per 100 cc	20.0	6-45
Water	100 cc	20.0	1.0

Numerous factors influence the viscosity of rubber in solution, such as the extent of mastication of the rubber and the effect of various fillers and addition agents. These will be brought out in a review of the rubber cements. Another factor not usually appreciated in the preparation of rubber cements is the influence of oxygen during plasticization or mechanical breakdown of the rubber before mixing with a solvent to form the cement. Fry and Porritt measured the change in solution viscosity after different periods of heating thin rubber sheets at high temperatures and after milling them mechanically at high temperatures. Some of their results are shown in Figure 26. The solution viscosity of the rubber as a function of temperature and time of milling indicated that molecular degradation due to oxygen absorption was the most important factor contributing to lower solution viscosity<sup>60</sup>. Bruce and Blake pointed out

further that tackiness of rubber adhesives is due largely to the action of light and oxygen<sup>61</sup>; hence the adhesive properties of rubber cement will be influenced to a large extent by this phase of its history. Houwink also reviewed the oxidation of rubber, pointing out that in many experiments the amount of oxygen present is in question<sup>62</sup>. Stephens and associates also produced a number of solutions of greatly reduced viscosity by catalytic oxidation<sup>63</sup>.

Before reviewing the preparation of solvent types of rubber cements, the influence of vulcanizing ingredients and the processes of vulcanization should be examined. Vulcanization is essentially a process which reduces the plastic properties of the rubber and increases the resistance to the swelling effect of solvents. This means that unvulcanized rubber, when

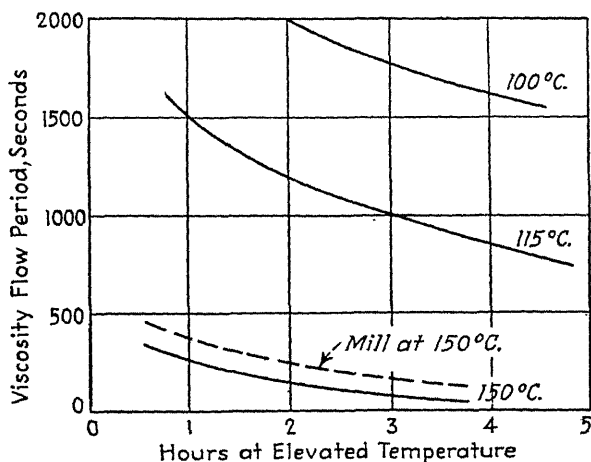
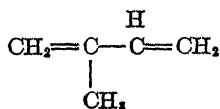


Figure 26. Effect of milling at high temperature on viscosity of rubber solution

stretched, will not return as rapidly as or to the same degree as vulcanized rubber when elongated. While a complete explanation of vulcanization in the light of experimental data is not yet available, it is generally accepted that molecular cross-linking through chemically combined sulfur is the most important phenomenon. Weber is generally credited with first suggesting the concept of chemical linkage between rubber and sulfur<sup>64</sup>.

The structure for isoprene, basic structural unit in natural rubber, is generally accepted as follows:





The influence of accelerators for vulcanizers was felt not only in mechanical rubber goods, but also in their adhesives. Russell for example prepared rubber cements with the aid of sulfur, zinc oxide, and an ultra-accelerator<sup>73</sup>. Sutton explored various vulcanizable and non-vulcanizable cements, particularly with respect to their stability, as measured by their tendency to gel on standing<sup>74</sup>. He pointed out that maximum adhesion of the cement took place just before the mixed solution started to gel. Using the following combination he reported on time for adhesion (open assembly time) and gel time of the activated cement (pot life), for different types of rubber:

Self-Vulcanizing Cement		Grade of Rubber	Gel Time (min)	Adhesion (mins.)
Rubber	100	Evaporated Latex Smoked Sheet Pale Crepe Para (washed)		
Zinc Oxide	5		24	190
Tetramethylthiuram			30	195
disulphide (accelerator)	1		33	160
Sulphur	2		72	193
Benzene	1000			

A typical automobile tire repair cement would contain 10 to 12 per cent of para rubber masticated in gasoline or benzene with 1 to 2 per cent of rosin to enhance the adhesiveness. The non-elastic gutta percha has also been employed in rubber cements in combination with asphalt and mineral oil as softeners<sup>75</sup>. Lloyd prepared permanently tacky adhesives from 5 parts of rubber and 1 part of gutta resin or Balata resin<sup>76</sup>. Meyer mixed pure fatty acids and plasticizers with rubber below 200° to form a rubber cement<sup>77</sup>. Marlett combined 3.75 lbs of resin, 1 lb of coal-tar pitch, and 1/2 lb of linseed oil, with 1/5 lb of vulcanized rubber and 1.5 lbs of 60°Bé gasoline<sup>78</sup>. Cameron developed an adhesive for stone and concrete comprising animal glue, flour, and a rubber solution<sup>79</sup>. Rubber solutions combined with nitrocellulose are also reported as useful coatings and adhesives. Tetrahydronaphthol acetate and other plasticizers are employed in their formulation<sup>80</sup>. Semon reported the preparation of rubber adhesives from vulcanized rubber fluxed with an equal quantity of ester gum and dissolved in carbon tetrachloride or gasoline<sup>81</sup>. Hale developed an adhesive sheet material from gutta percha, an adhesive agent, and plasticizer<sup>82</sup>.

Zimmerli and Havenhill prepared a solution of calcium resinate, rosin, and rubber in preparing a cement. Reclaimed rubber was employed throughout<sup>83</sup>. Obst mentioned rubber, shellac, and carbon disulfide as a useful marine glue<sup>84</sup>. Comminuted chrome-tanned leather and vulcanizing ingredients added to rubber in an organic solvent prepared a superior

type of rubber adhesive<sup>85</sup>. Prolonged milling and aging of natural rubber accompanied by the addition of coumarone-indene resin form the basis of various rubber adhesives, according to Malone<sup>86</sup>. McCortney added calcium resinate, rosin, and an organic peroxide to rubber to prepare adhesive products. The role of the benzoyl peroxide used was to effect some depolymerization of the rubber<sup>87</sup>. Blends of shellac and rubber make useful adhesives. The hardness and elasticity may be controlled by various proportions though as much as 40 per cent of shellac may be present<sup>88</sup>.

Drew prepared a number of pressure-sensitive adhesives for transparent and cellulosic masking tapes. The adhesives were applied to creped paper or to cellophane. The problem was to develop a film which would promote adherence of the tape to a wide variety of surfaces, though the adhesive film would not leave any deposit or offset upon the surfaces against which it had been pressed. For the best adherence of the pressure-sensitive adhesive layer to the backing, a primer coat on the tape was recommended<sup>89</sup> consisting of one of the following:

Primer Coats			
A		B	
Rubber	2	Tire tube reclaim	9
Pine wood pitch rosin	4	Crepe rubber	1
Whiting	1	Wood rosin	140
		Whiting	40

The adhesive film layer comprised one of the following:

Adhesive Layer.			
Crepe rubber	10	Double breakdown crepe	20
Coumarone-indene	2	Paracoumarone resin	8.5
Zinc oxide	$\frac{1}{2}$	Wood rosin	1.0
		Liquid paraffin oil	0.5

Additional adhesive films were described by Drew as consisting of raw rubber 1.0 parts and low acid ester gum 0.2 to 4 parts dispersed in heptane and alcohol. The highly coherent transparent adhesive was suited to glass and cellulosic films<sup>90</sup>. The degree of adhesiveness was determined by the amount of milling, and it was recognized that the more severe the milling the less ester gum was required. The acid number of the ester gum employed was 2 to 10. Better aging was reported with the ester gum as the tackifier, rather than rosin. Addition of alcohol solvent helped to reduce the viscosity. The adhesive tapes for which these rubber cements were intended included numerous masking tapes widely used as seal-offs for lacquers and temporary holding action<sup>91</sup>. In addition to the above formulations a good adhesive layer was obtained by milling together

plantation rubber and Mexican guayule rubber, which is high in natural resin content. In other adhesive tapes a parchmented surface was applied on one side and a partially vulcanized rubber adhesive was applied to the other side<sup>92</sup>. In a permanently tacky adhesive pale crepe rubber, gutta resin, and an acetone-aniline condensation product are employed<sup>92a</sup>.

Charch and others developed a large number of adhesives for bonding vulcanizable rubber to regenerated cellulose tire cords, such as are employed as reinforcement in the manufacture of automobile tires. Among the many materials suggested for association with the vulcanizable rubber latex were: Amine-aldehyde resinous condensation products, polyvinyl alcohol, ketone-aldehyde, phenol-aldehydes, and deacetylated chitin<sup>93</sup>.

Little covered the art of applying tackifying agents such as ester gum, rosin, dammar gum, manila gum, coumarone-indene resins, and hydrogenated rosin to rubber adhesives, in conjunction with plasticizers such as hydrogenated ethyl abietate or hydrogenated benzyl abietate<sup>94</sup>. Among the pressure-sensitive adhesive formulations described were:

Hydrogenated methyl abietate	34	Hydrogenated ethyl abietate	40
Rubber	6	Rubber	10
Rosin	60	Hydrogenated rosin	50

Pragoff developed improved adhesives involving rubber and rosin derivatives. He pointed out that inasmuch as rosin is an unsaturated acid, it is quite susceptible to oxidation and that when exposed to atmospheric conditions rubber-rosin base adhesives deteriorate and lose their adhesive qualities. Consequently in place of rosin, he employed a heat-treated rosin, processed in the presence of nickel, platinum, or copper chromite catalysts which effect an intramolecular rearrangement to yield compounds rich in dehydroabietic acid. These acids or their esters present to the extent of 20 to 30 per cent of the weight of the rubber yield adhesives which have good age resistance and retain their tack and adhesion<sup>95</sup>. In further adhesives, Pragoff employed 40 to 60 parts of rubber, 80 to 20 parts of dehydrogenated rosin and 10 to 15 per cent of lanolin<sup>96</sup>.

As an aid to metal bonding of rubber, Domm pointed out that zinc coating on a steel wire followed by a thin copper coating, permitted satisfactory bond to vulcanizable rubber<sup>97</sup>. He claimed that the zinc and copper alloyed to form a brass coating quite receptive to good adhesion to the rubber. The thickness of the copper was approximately 0.000016 inch. Scholl claimed that the addition of a small amount of sulfide of phosphorus or red phosphorus to the rubber improved the bond to metal<sup>98</sup>. Pierce pointed out the advantages of a thin coat of coumarone-indene resin on the metal wire in securing a good bond to the rubber<sup>99</sup>.

Drew prepared an improved adhesive masking tape of less hygroscopic character than his earlier types by impregnating a porous paper backing with a composition of 100 parts of milled rubber, 75 to 125 parts of zinc oxide, and 140 to 180 parts of rosin in an organic solvent such as heptane. To this was coated a pressure-sensitive, non-offsetting adhesive<sup>100</sup>. Saunders and Morrison prepared a number of valuable adhesives from rubber by fusing together rubber, rosin and asphalt or distillation residue from triglyceride-containing oils. This was conducted above the devulcanization and depolymerization temperature of the rubber to flowing consistency. Sulfur was added and the product dispersed in a volatile solvent<sup>101</sup>. In further developments along the same line Saunders and Morrison specified the use of "Petropol", described as a plasticizing tackifier. "Petropol" is a hydrocarbon polymer resulting from the polymerization of the diolefin constituent of a hydrocarbon distillate. They are obtained by high-temperature cracking of hydrocarbons above 750° and are characterized by a high degree of unsaturation. In fusing the batch together in preparing the adhesive, 33.5 lbs of asphalt, 7.1 lbs of rosin, 7.1 lbs of ester gum, and 23.8 lbs of "Petropol" are heated to 250° and 28.5 lbs of rubber scrap are added in small increments over a twenty minute period. After stirring and further heating the batch is cooled to 110° and various fillers may be added. The batch may be cut with various solvents such as naphtha or compounded further with other rubbers or tackifiers<sup>102</sup>. Saunders has recently attracted much attention in the development of "Cycleweld" adhesives for metal parts; these have very high shear strengths in aluminum-to-aluminum bonds<sup>103</sup>. Though their chemical identity is not disclosed, they are broadly classified as rubber-resin combinations.

Abrasive compounds come in for their share of rubber adhesives. Martin describes one in which the granules are coated with rubber as an organic bond, with added sulfur and an inert filler to at least 25 per cent of the bond volume<sup>104</sup>. Rubber-bonded abrasive grinding wheels are well known commercially. Adinoff described a number of cements prepared from reclaimed rubber, rosin, lime, and naphtha<sup>105</sup>. Conover reviewed current methods of digestion processes<sup>106</sup>. He also discussed problems of reclaiming synthetic rubbers for which monocarboxylic acids were described as useful.

Groskopf worked on rubber cements which were sprayable without cob-webbing, stringing out in fine fibers when applied from a spray gun, employing 3 to 10 per cent of water-swollen powdered clay<sup>107</sup>. The rubber is sprayed from an organic solvent. Geiger observed that "Nypene", a terpene polymer, imparts tackiness to rubber adhesives. A minimum loss of elasticity before vulcanization was claimed by the use of these additives<sup>108</sup>. Marks prepared a waterproof adhesive composition for the

manufacture of spiral or convolute wound paper containers. To 10 parts of masticated rubber he added 160 parts of rosin, copal, senegal gum, or Manila gum, dissolved in a water-miscible organic solvent for the rubber and resin. To this he added an alkaline aqueous solution of 6 parts of a second resin of lower acid number than the first and 10 to 30 parts of casein<sup>109</sup>.

Kutz developed a technique of preparing a low viscosity cement by boiling rubber in carbon tetrachloride for two hours in the presence of copper<sup>110</sup>. Lloyd prepared a transparent adhesive from pale crepe rubber, resinous guttapercha, balata, antioxidant, and solvent<sup>111</sup>. A rubber cement-rubber latex combination was prepared by Riefenstahl, with a continuous phase of rubber swollen by solvent, together with a rubber latex and petroleum rubber solvent containing 2 to 5 per cent of rosin<sup>112</sup>. Terpenes such as beta-pinene have been proposed as tackifiers for rubber cements. Mineral oil is also blended at 80–150°<sup>113</sup>. A plasticized rubber mass is treated with a soap of a multivalent metal and coumarone-indene resins at least equal in weight to the rubber<sup>114</sup>, forming a rubber adhesive product. Twiss and Neale prepared a permanently tacky adhesive forming a semi-solid emulsion with water as a discontinuous phase<sup>115</sup>. Harkins prepared a synthetic resin-rubber adhesive by dissolving rubber with a soluble phenolformaldehyde resin and lead chromate in an organic solvent<sup>116</sup>. Hershberger found improved adhesion between a solid structure and rubber by treating the surface with a tannin-amine reaction product and then vulcanizing<sup>117</sup>.

Considerable work has also been done in the proper proportioning of solvents for rubber cements, and the literature is replete with examples. For example, Blocker employed a 5 per cent rubber solution in 95 per cent of naphtha with equal parts of ether and benzene, and 3 per cent of chloroform<sup>118</sup>. Hazell employed ethyl alcohol in naphtha to help reduce the viscosity of rubber cements<sup>119</sup>. In considering these and other examples of viscosity control through solvents, it must be borne in mind that the previous history of the rubber is perhaps the most influential factor. Slomon controlled the tackiness of his rubber-ester gum adhesives by incorporating therein a mixture of ethyl and butyl acetate<sup>120</sup>.

In the preparation of adhesive sheetings, Morgan developed some effective solvent combinations<sup>121</sup>. Employing a pressure-sensitive coating of rubber 60 to 70 per cent of pale crepe, 25 to 30 per cent of resin (dammar gum, coumarone, or rosin) and 0.1 to 1.0 per cent of phthalic acid in solvent to eliminate odor, he utilized dihalogen-substituted ethyl ethers, together with the other solvents. Clear adhesive films were formed. A typical solvent combination included 70 to 80 parts of gasoline, 20 to 25 parts of benzene, and 4 to 10 parts of *bb'* dichloroethylether. Solutions

of rubber in paraffin wax were effected at 120–140° in conjunction with pale crepe rubber. Butyl methacrylate was mentioned as a stabilizer<sup>122</sup>. Rubber and asphalt, limed rosin, and a plasticizing agent having a pep-tizing action on rubber are employed in another rubber adhesive<sup>123</sup>. Cashew nutshell oil, plus another phenol and depolymerized vulcanized rubber are dissolved in a solvent and applied as a useful adhesive<sup>124</sup>. Solvents with a major proportion of branched chain paraffins (5 to 9 C-atoms) are recommended for rubber cements<sup>124a</sup>.

Campbell discovered that rubber cements with a halogenated nitro-paraffin containing less than 8 carbon atoms greatly retarded the gelling of vulcanized cement on standing<sup>125</sup>. The solvent, 1-chloro-1-nitropropane is mentioned in particular as a stabilizer. Using a rubber cement formulated in two parts:

Part A		Part B
Rubber	100	100
Zinc oxide	10	
Sulphur	6	
Zinc dibutyl dithiocarbamate		1
Polybutyraldehyde aniline		1

Part A added to part B forms the cement. Dispersed in various solvents the time for the adhesive to gel was noted by Campbell as follows:

Nitroparaffins as Stabilizers for Rubber Cements.  
(Hours at 50°C. Before Gelling.)

Nitroparaffin Addition		Benzene	Naphtha	Ethylene Dichloride
None		33.5	144	87
1-chloro-1-nitropropane	1%	63.5	201	284
	5%	162.0	411	284
	10%	421	411	284

The nitroparaffins similarly inhibit the gelling of synthetic rubber cements formulated of Buna-S and Hycar-OR, greatly extending the shelf life after activation. It should also be remembered, however, that drying time and open assembly time of the adhesive may be affected.

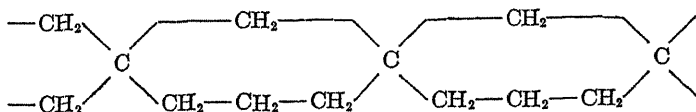
In a few further examples of the applications of rubber cements to adhesive tapes and sheetings, the work of Thies may be noted; he employed a starch-impregnated fabric sheet, in conjunction with a cured rubber sheet, surfaced on one side with gum rubber and a cold patch cement on the other side<sup>126</sup>. Crawford also improved the adhesion of rubber to cotton fabrics by treating the cotton with a shellac-amine soap, applying the vulcanizable rubber and vulcanizing the assembly<sup>127</sup>. In cementing rubber-impregnated fabric to fabric free of rubber it has also proved desirable to soak the fabric in a volatile rubber solvent for a few minutes<sup>128</sup>.

## CYCLIZED RUBBER CEMENTS

The cyclization of rubber with strong acids or acid-forming salts has led to the development of a number of useful thermoplastic derivatives of rubber capable of forming the basis of strong adhesive formulations. A somewhat complex reaction ensues as rubber and various acids are brought together. Thies cited the work of Leonhardi, who in 1781 referred to a tough, elastic product of sulfuric acid on rubber<sup>129</sup>. However, in this country, the early work of Newbrough in the preparation of what is usually referred to as "Newbrough" rubber, initiated industrial attention. He prepared a combination of two parts of turpentine with one part of sulfuric acid, which after cooking together was admixed with rubber. After the two were thoroughly blended they were molded at 150° for about an hour to obtain a hard product totally different from rubber<sup>130</sup>. However, his work did not make specific reference to adhesive applications.

Sheppard prepared a rubber adhesive by treating rubber with sulfur chloride<sup>131</sup>. He prepared an adhesive solution by dissolving 2 lbs of rubber in 6 gallons of carbon tetrachloride. To this he added 10 cc of sulfur chloride dissolved in 1000 cc of acetone and 1200 cc of amyl acetate. The sulfur chloride is substantially a vulcanizing agent in this application. However, the real origin and understanding of cyclized rubber is generally attributed to Fisher<sup>132</sup> and Kirchhof<sup>133</sup>, who independently obtained a number of thermoplastic materials by milling rubber with sulfuric acid. Actual commercial developments took place by heating the rubber on a mill at 130° for a number of hours with organic sulfonic acids, chlorosulfonic acid, or sulfonyl chloride. The end products are the well-known "Thermoprenes". Their physical properties depend on the time and temperature of heating, varying from rubbery thermoplastics to hard, shellac-like materials, which are much more saturated than the original rubber. They have found wide application in bonding rubber to other materials. These synthetic isomers of rubber (they have the same empirical formula  $(C_6H_8)_x$ ), resemble the natural isomers of rubber, balata and gutta-percha in many ways.

The process of cyclization of the rubber with the strong acids is generally depicted in the following manner:



Solutions of the cyclized rubber are much lower in viscosity than the natural rubber solutions. Bruson, Sebrill, and Calvert produced rubber isomers which have shown a large decrease in unsaturation and some interesting adhesive properties<sup>184</sup>. They prepared their products by treat-

ing rubber with antimony pentachloride, stannic chloride, ferric chloride, chlorstannic chloride, or titanium chloride in an inert nitrogen atmosphere. In particular, chlorstannic acid is used in preparing these isomers, for example, by adding about 10 per cent direct to rubber on a mill or to a benzene solution of rubber<sup>135</sup>. They claimed the formation of an addition product with stannic chloride. The following structural formula is gen-

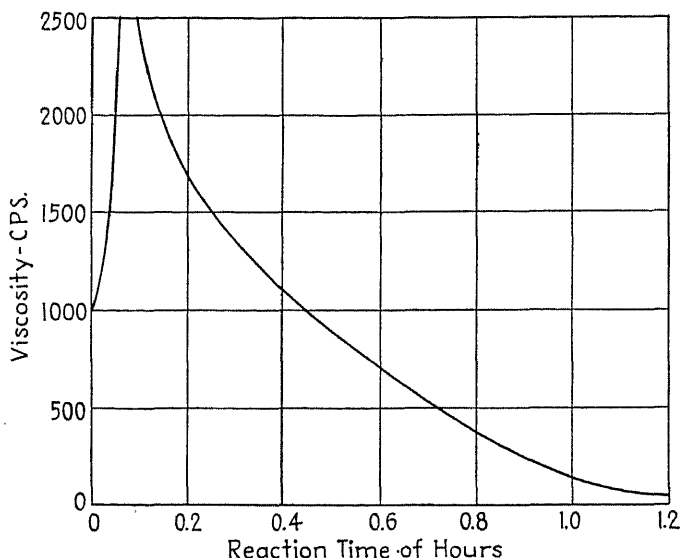
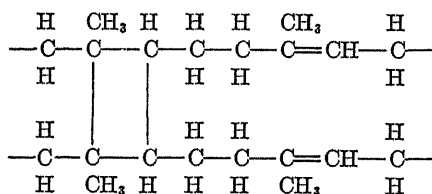


Figure 27. Cyclization of rubber with chlorstannic acid, change in viscosity

erally proposed for the rubber isomer prepared from stannic chloride or chlorstannic acid:



When rubber is cyclized with stannic chloride or chlorstannic acid there is an immediate increase in solution viscosity. Thies demonstrates, how the final viscosity may be as little as 1/1000th of the original solution viscosity upon completion of cyclization. One of the curves showing reaction time as a function of viscosity is depicted in Figure 27<sup>136</sup>. Peak viscosity is reached within one or two minutes after adding the reagent.

In one hour the viscosity in this reaction will decrease from 1 poise to 0.03 poise. When reagent is added the viscosity is approximately 36 poises.

Geer also employed compositions of the following chemical structure as isomerizing agents:— $R-SO_2-X$  where X was OH or halogen, and R an organic radical with an OH group<sup>137</sup>. In further work, Fisher reduced the amount of strong sulfuric acid he employed in reaction upon rubber<sup>138</sup>. He specified 2 to 25 parts by weight of sulfuric acid (specific gravity 1.84) per 100 parts by weight of rubber. Control of final properties is exercised by the amount of acid mixed with the rubber. Further rubber isomers are prepared by milling aluminum, antimony, and iron salts in with the rubber at 200 to 250°<sup>139</sup>.

Geer prepared adhesive products by heating rubber with *p*-phenolsulfonic acid to form tough, balata-like isomers of rubber<sup>140</sup>. Others prepared rubber isomers by first creaming rubber latex with a weak organic acid, followed by the addition of strong acid such as sulfuric, benzenesulfonic acid, chlorosulfonic acid, heating to remove volatiles, and baking. A protective colloid such as casein or glue may be added during creaming<sup>141</sup>. The formation of rubber isomers in the presence of naphtha or benzene solvents by the action of sulfuric acid, sulfonic acids, stannic chloride, or phosphoric acid has also been recorded<sup>142</sup>. Even nitric acid was proposed as a cyclizing agent for rubber, by heating to 200–350° to form an adhesive mass<sup>143</sup>.

Twiss, Jones, and Anderson prepared adhesives by concentrating upon resinous by-products extracted from rubber, balata, and gutta percha and treating them with sulfuric acid, sulfonic acids, or stannic chloride in the presence of rubber<sup>144</sup>. In a typical example, 70 parts of the semi-fluid resin obtained by extracting crude balata with a petroleum solvent are heated for several hours with 30 parts of thinly sheeted smoked rubber. When a smooth solution is formed, 4 parts of hot phenolsulfonic acid is added. The reaction mixture is maintained at 110° for five hours. Dissolved in toluene (20 per cent solution), a good rubber-to-metal adhesive is obtained. In addition, by heating the solid adhesive with oleic acid and casein, and slowly adding dilute ammonia solution, water-dispersed adhesive is obtained.

Banbury, Clarke, and Evans prepared further modifications of rubber by treating the latex with a stabilizer and then adding a strong acid. The residue was baked and the solid reaction product dissolved and employed as a binder for paper and abrasive grains as in the manufacture of sanding wheels<sup>145</sup>. Further developments along parallel lines were forthcoming in the work of Clarke, Shepherdson, and Robinson, who creamed latex in the presence of glue or casein and added sufficient sulfuric acid or benzene sulfonic acid to effect coagulation. After removing volatiles the end prod-

ucts were baked at 150° to form rubber isomers of the type useful for cements or adhesives<sup>146</sup>.

Sulfur chloride dispersed in a mass of crude, solid rubber if heated to convert to a soft and sticky plastic, has been suitable for use as an adhesive material according to Gray<sup>147</sup>. Presumably free hydrochloric acid was formed to react upon the rubber molecules to form the thermoplastic isomers. Sebrell dissolved pale crepe rubber in benzene and added 10 per cent of chlorostannic acid ( $\text{H}_2\text{SnCl}_6 \cdot 6\text{H}_2\text{O}$ ) based on the weight of the rubber. The reaction was terminated by the addition of water, which also decomposed the addition product formed with the isoprene units<sup>148</sup>. He also introduced a reducing agent such as hydroquinone or sodium sulfite into the water to nullify oxidation effects, which affected the solubility of the rubber isomers. This same principle Sebrell invoked in preparing further adhesives, by dissolving rubber in benzene, reacting stannic chloride thereupon to form an addition product, and drying in the absence of air<sup>149</sup>. Various coatings can be prepared from these materials, coatings which will oxidize in air and become insoluble in aliphatic hydrocarbons.

Twiss and Jones compounded rubber, gutta percha, or neoprene with a compound containing  $\text{SO}_3\text{H}$  or capable of forming it (sulfuric acid, sulfonic acids, etc.). These were milled, then heated at 110° for twenty hours, and milled again. When dissolved in  $\text{C}_6\text{H}_6$ , they formed the basis of a useful adhesive<sup>150</sup>. Thies evaluated the properties of cyclized rubber from stannic chloride or chlorostannic acid, in combination with pure rubber. In determining the various physical properties, the stiffening action of the cyclized rubber was readily observed<sup>151</sup>. Rubber and cyclized rubber in combination with waxes have formed the basis of adhesives for paper products<sup>152</sup>. These could be heat-sealed at 200–400°F. One formulation comprised: 40 to 60 parts of wax, 10 to 30 parts of rubber, and 20 to 40 parts of cyclized rubber. In an examination of cyclized rubber derivatives, Endres pointed out that the typical physical properties of rubber cyclized with 7.5 per cent *p*-phenolsulfonic acid were<sup>153</sup>: specific gravity, 0.980; tensile strength, 2600 psi; elongation at break, 27 per cent.

This particular reaction product has been widely used as an adhesive, Endres points out, particularly for metal to rubber. It may be vulcanized to rubber products by incorporating a small percentage of sulfur. Of the chlorostannic acid reaction products, those of relatively low softening point are suited to formulation of various metal adhesives, though the harder varieties are largely used as coating materials. Outstanding resistance to acids and alkalis has been one of the unusual properties of such coatings. Thies described in detail the properties of the chlorostannic acid reaction products upon rubber, particularly as a coating material for

paper and cloth<sup>154</sup>. Such coatings may be readily heat-sealed to one another through the action of temperatures of 150°. In manufacturing commercial grades of material, a high-grade, low-protein content rubber is employed as the starting point. Reaction products with a wide range of softening points (25 to 105°, "Pliolite") are obtained as a fine powder from the solvent. Adhesive grades are selected from materials softening at 55 to 65°. The materials are milled before dissolving them in solvents. Thies lists the relative viscosities of rubber cyclized with chlorostannic acid and drying time of the films; the viscosity obtained with a Ford No. 4 cup with relative orifice at 22-24° is reported herewith:

Table 14

*Relative Viscosities and Drying Times of 20% by Weight Chlorostannic Acid. Reaction Products in Various Solvents at 22-24°C. and 23-30% Relative Humidity.*

Solvent	Viscosity (Secs.-Ford No. 4 cup)*	Drying Time .001" film (mins)
High-test gasoline	1.00	3.0
"Skellysolve D"	1.13	3.25
Xylene	1.68	13.50
Benzene	1.70	1.5
Solvesso No. 2	1.92	38.5
Varnish makers' naphtha	2.0	53.0
Kerosene	4.53	1530.0
Turpentine	6.0	28.5
Carbon tetrachloride	35.1	4.5

\* Sci. Inst. Co. of Detroit.

Swart described a number of lap joints of metal bonded to rubber with various rubber cements, including the thermoplastic rubber isomers<sup>155</sup>. These techniques were employed in the manufacture of doors for airplanes and automobiles. Resins prepared in the presence of strong acids may be polymerized at the same time that the rubber is being cyclized. This has been practiced by polymerizing coumarone-indenes in the presence of rubber and sulfuric acid<sup>156</sup>.

Ladd and Rakas prepared rubber cements by the action of 1 part of perchloric acid on 6 parts of a 20 per cent solution of crepe rubber. On heating at 49-65° the solution viscosity was considerably lowered<sup>157</sup>. The isomer of rubber formed was precipitated with ethyl alcohol, neutralized with sodium hydroxide and dissolved in four volumes of carbon tetrachloride or benzene, for use as rubber cement. Reid succeeded in effecting improvements in rubber adhesives which do not require hot vulcanization by combining rubber isomers (from sulfuric acid and rubber) with an oxidizing and vulcanizable agent, such as tetrachloroquinine<sup>158</sup>. He reported that in ASTM tests on the bonding of rubber to metal, strengths of

300 psi were obtained with soft rubber and 2500 psi between hard rubber and steel.

Reaney developed rubber-to-metal bonds by two or more superposed thin films of rubber isomers decreasing in hardness<sup>159</sup>. In other developments of rubber to metal bonds, Reaney prepared several hydrocarbon rubber derivatives by milling together solid rubber, weak acids, and solid salts of strong acids. For example, solid aluminum sulfate, alum, or acid sulfate and one or more of the group of phosphoric acid, phosphorus pentoxide, or acetic acid were milled with rubber into  $\frac{1}{4}$  inch sheets at 100–150°<sup>160</sup>. Griffith bonded rubber and metal parts together with membranes rubber conversion product layers<sup>161</sup>. Rubber cements have also been prepared from equal proportions of rubber and cyclized rubber, with channel black<sup>161a</sup>.

A non-sulfur chemical (aromatic acyl peroxides or halogenated quinones) possessing the properties of oxidation and vulcanization has been added to rubber isomer-based adhesives with good results<sup>162</sup>. Adhesives which resist oils are prepared from rubber and maleic anhydride and a saturated monohydric alcohol (2:1:4 ratio) with organic peroxides as catalysts<sup>163</sup>. It is not always necessary to use cyclized rubber as the adhesive agent in bonding two sheets of rubber together, as in some circumstances very effective results may be obtained by cyclization of the rubber surface just before applying the adhesive, which may be a thermosetting synthetic resin. Cyclization of the rubber surface is accomplished by treating the rubber with concentrated sulfuric acid for 5 to 10 minutes and then thoroughly washing to remove the acid. The rubber surface conditioned in this manner will have a much more effective bond than one not treated.

### Phenol-modified Rubber Adhesives

Treatment of rubber with strong acids in the presence of phenol has been observed by Fisher to yield strongly adhesive products<sup>164</sup>. For example, phenol and hydrochloric acid are added to a solution of rubber (5 per cent in benzene) and heated for a long time. The product, after washing to remove traces of acid, is suitable for coatings and for adhesives. Fisher reports that in metal-rubberized fabric assemblies this adhesive is 10 to 15 times as strong as the best rubber cements. He also prepared mixtures with chlorinated rubber and rubber hydrochloride.

In other developments by Fisher, phenol, pyrocatechol, and acid were reacted to form various thermoplastic derivatives from rubber<sup>165</sup>. The phenols in this case have been looked upon as catalysts. Phenol-furfural and rubber were used by Thompson in bonding vulcanized rubber to metal under heat and pressure<sup>166</sup>. Ford included an aldehyde together with

phenol in the preparation of rubber isomers. He heated mixtures of rubber, aldehyde, phenol, and an isomerizing agent. The products were soluble in benzene and hard at room temperatures<sup>167</sup>, though rubbery at 75°.

Williams examined a large number of phenols in combination with rubber and produced a group of thermoplastic derivatives of phenol-modified rubber, which found early acceptance primarily as adhesive materials<sup>168</sup>. Mixtures of unvulcanized rubber, certain phenols, and catalysts were reacted to form a thermoplastic material having none of the characteristics of the original rubber and distinguished by lack of adhesion to unvulcanized rubber. A chemical combination of the phenol with the rubber is suggested. Among the phenols examined were phenol, *p*-chlorophenol, *o*-cresol, *p*-phenyl phenol, beta and alpha naphthol, and others. Beta-naphthol appeared to be the most satisfactory and was preferred over the others.

Reaction between the phenols and the rubber is greatly aided by the presence of small proportions of catalysts such as sulfuric acid or halogen sulfonic acids. From 2 to 50 per cent of the catalyst based on the phenol is used, with a preferred range of 20 to 50 per cent. The reaction is quite exothermic, and products with softening points of 50 to 110° are obtained. Solubility in benzene, toluene, and gasoline is characteristic of the materials. Not all the phenol chemically associates with the rubber, 1 to 5 per cent being estimated from extraction tests, while the balance is generally free and capable of association with aldehydes. Of the catalysts, mixtures of sulfuric acid with the alkyl sulfates appear to offer certain advantages in conducting the reaction. Williams claims that this reaction takes place in a much shorter time than in preparation of other thermoplastic derivatives of rubber, and that a purer end product is obtained.

Mitchell concentrated on the adaptation of the phenol-modified rubber as an adhesive for plain and moisture-proofed regenerated cellulose sheets and tapes. He pointed out that considerable time and money have been spent in trying to develop adhesives particularly for moisture-proofed regenerated cellulose, so important to fulfilling sealing requirements when the sheets are used for wrapping purposes. Mitchell points out that the phenol-modified rubbers, particularly the beta-naphthol-modified type, possess an adhesion to smooth surfaces far superior to other rubber derivatives. For example, excellent bonds are obtained between the regenerated cellulose and the pressure-sensitive rubber adhesive film of the type described earlier in this chapter, by the use of an intermediate bond of phenol-modified rubber. A typical composition is prepared by milling together 20 parts of beta-naphthol, 4 parts of sulfuric acid, and 100 parts of rubber until the reaction is complete and extracting the excess beta-naphthol. Typical pressure-sensitive adhesives may consist of<sup>169</sup>:

Beta-naphthol-modified rubber,	4	Beta-naphthol-modified rubber,	10
Chlorinated diphenyl (62% Cl),	4	Pale crepe rubber,	10
Chlorinated paraffin wax (35% Cl),	1	Rosin,	18
Toluene,	14	Chlorinated paraffin wax (35% Cl),	5
		Toluene,	100

Mitchell prepared further rubber derivatives by reacting maleic anhydride with cyclized rubber<sup>170</sup> and also with phenol-modified rubber at 60 to 150°; from 1 to 5 per cent of phenol is chemically combined<sup>171</sup>. Red-farn simultaneously treated rubber with maleic anhydride and phenol at the boiling point of the latter<sup>172</sup>. Popham dispersed rubber in phenol at 140–150°C, passing oxygen through until rubber dissolved. The material was then reacted with formaldehyde to form an adhesive resin<sup>172a</sup>. In somewhat parallel developments, Gross combined phenol-furfural with rubber to form a stable adhesive<sup>172b</sup>; while others have combined depolymerized rubber with a phenol-formaldehyde resin<sup>172c</sup>. A large number of other adhesive formulations were prepared involving cyclized and phenol-modified rubber<sup>173</sup> including:

- (1) Cyclized rubber plus unsaturated acids (acrylic acid, methacrylic, crotonic, itaconic, cinnamic, etc.)
- (2) Beta-naphthol rubber plus unsaturated acids.
- (3) Phenol-modified rubber plus polyisobutylene and wax.
- (4) Cyclized rubber plus polyisobutylene and wax.

Popham prepared adhesives from oxidized rubber and maleic anhydride with oxalic acid catalyst and added phenol; the whole was heated in an oxidizing gas and reacted with formaldehyde<sup>174</sup>.

Hiers prepared some rubber cements with the aid of finely divided calcium carbonate, calcium silicate, and aluminum hydroxide, less than 1 micron in diameter, with phenol-modified rubber<sup>175</sup>. Harmon reported considerable improvement in the aging characteristics of phenol-modified rubber adhesives by incorporating amino-type polymers, which exert a stabilizing effect<sup>176</sup>. Typical phenol-formaldehyde methyl amine resins have been described<sup>177</sup>. For example, to 25 parts of phenol modified rubber (1 to 5 per cent phenol chemically combined), is added 6.2 parts of a phenol-formaldehyde methyl amine resin, in 81.2 parts of toluene. Excellent adhesion is reported for wood and metal foils. In another example, the following proportions were reported:

Diphenylguanidine-formaldehyde resin	10
Beta-naphthol-modified rubber	40
Paraffin wax	10
Chlorostannic acid-rubber reaction product	40

In reporting on a series of aging tests, Harmon presented the following table<sup>176</sup>. In measuring the stabilizing effect of the amino polymer, the

Table 15  
*Stabilizing Effect of Amino Polymer*

Material	Amino Polymer	Force in Grams to Break Bond after				
		0 days	7 days	14 days	28 days	42 days
Phenol-modified rubber Paraffin wax	90 10 None	700	30	20	10	10
Ditto plus dimethyl amino ethyl methacrylate	3 parts	700	600	600	600	600
Ditto plus diphenyl guanidine-formaldehyde	3 parts	700	640	110	—	—
Ditto plus phenol-formaldehyde piperazine	3 parts	700	650	650	650	650

heat seal bond strength was evaluated as the force in grams (rolling shear) to strip a tape back after aging at 35° for various periods of time (see table). Geer also reported amines as age resisters for rubber isomers used in the manufacture of adhesives<sup>178</sup>.

Experiences with the phenol-modified rubbers are still relatively new as compared with the cyclized rubbers, though they have shown promise of playing an increasingly important role in the adhesives field. Also it must be realized that much of the work on the cyclization of rubber and the formation of thermoplastic derivatives has been applied to natural rubber. Similar work is already in progress on synthetic rubbers, and to all appearances the industry is just at the beginning of important activities in the development of plastic products from rubber-like materials.

### Oxidation Effects on Rubber Products

Analysis and understanding of the effect of oxidation on rubber products appear in an immature state as compared to other activities on rubber derivatives, though they merit attention in studying the processes of adhesion. Earlier investigators examined the effect of oxygen or oxidizing agents in lowering the viscosity of rubber solutions. Stephen's work in lowering the viscosity of rubber adhesive solutions by catalytic oxidation has already been noted<sup>83</sup>. One of the first agents employed on a benzene solution of rubber was an alkaline permanganate solution. Harries inferred that some depolymerization had occurred<sup>179</sup>. Peachey studied the rate of absorption by rubber quantitatively and reported that one atom of oxygen was used up for each  $C_6H_8$  grouping in the molecule<sup>180</sup>, a point subsequently confirmed by other investigators.

Changes in the solution viscosity of rubber heated in air are generally recognized as due to degrading or depolymerization effects, which also explains the attainment of a tacky adhesive state. It is important to recognize these features because much of the earlier work in developing rubber adhesives empirically involved milling the rubber at elevated temperatures and achieving results which may be due in a large part to the influence of oxygen. For example, Meyer reported the development of strong adhesives by melting rubber, a resinous body, and pure fatty acid below 200°<sup>181</sup>. This effect was not confined to the natural rubbers by any means, inasmuch as the synthetic methyl rubbers heated in air to at least their melting point and then dissolved in organic solvents produced excellent adhesives<sup>182</sup>. Healy prepared good rubber cements by first subjecting crude rubber to a temperature of 165° and a pressure of 90 psi for 30 minutes. This rubber was slowly dissolved in 70°Bé gasoline until it attained a smooth consistency<sup>183</sup>.

Dunfield heated rubber at 180–300° for 10 to 20 hours, and then added solvent and vulcanizing agent to produce an adhesive. Exposure of the

rubber at the elevated temperature was for the express purpose of depolymerizing the material<sup>184</sup>. Various vulcanizing ingredients are also described, and the good adhesion between metal and rubber is brought out. Dunfield prepared an adhesive of the following proportions:

Melted rubber (as above)	25-75 parts
Cyclized "Newbrough" rubber <sup>180</sup>	72-25 parts

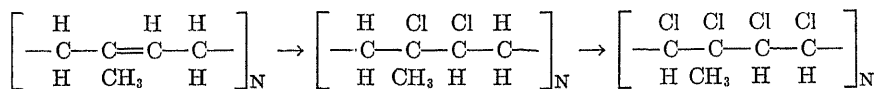
Stevens and Young oxidized rubber in solution with metallic oxidizing catalysts or with ozone at 50 to 90°. The products obtained were stated to possess good adhesive properties<sup>185</sup>. A formula of  $C_{10}H_{16}$  is ascribed to this product ("Rubbone"). Metal-to-rubber bonds have been effected with the aid of rubber solution, phenol-formaldehyde, and an oxidizing agent ( $O_2$  or  $PbO_2$ )<sup>186</sup>. Warden reviewed the role of organic peroxides in processing rubber, pointing out that deleterious effects may occur if the amount of peroxide is excessive<sup>187</sup>. He recommended relatively high processing temperatures to destroy unused portions of the catalysts. The observations by Houwink were brought out earlier in the chapter<sup>62</sup>. Smith prepared rubber adhesives by depolymerizing rubber through heat and oxygen. In one instant he combined this with rubber chloride, while in another example a partially reacted phenol-formaldehyde resin was introduced<sup>187a, 187b</sup>. In short, in considering the development of adhesives from rubber, the role of oxygen which may be absorbed during the process of milling or of heating alone, appears to be a significant contributing factor to the attainment of a proper balance of good adhesion and good cohesion.

### Halogenated Rubber Derivatives in Adhesives

Chlorinated rubber and rubber hydrochloride have long been prominent in the field of adhesives. Chlorinated rubber has been known for many years, having been prepared by direct chlorination of thin sheets or by chlorination of rubber in solution. Commercial grades of chlorinated rubber are available in different degrees of viscosity, which are determined by the initial average molecular weight of the rubber which was chlorinated. Rubber heated and milled a long time will have a relatively low molecular weight (about 25,000) as compared with the more usual types possessing a molecular weight of around 180,000. Much of the early investigations and development of chlorinated rubber took place abroad, and while a number of individuals contributed to the art during the last century, renewed interest was kindled by Peachey, who took out a patent for the manufacture of chlorinated rubber and prepared chemically resistant coatings and adhesives<sup>188</sup>.

The chlorination of rubber is depicted in steps, inasmuch as there is a decided evolution of HCl during the process. The commercial grades

contain an average of 67 per cent of chlorine, indicating that 3 to 4 chlorine atoms are present per isoprene unit. This is considerably more than would be expected if the chlorine added only to the double bond:



Commercially, rubber is usually chlorinated in solution and the product made available as a white, amorphous powder. Chlorine is passed into a  $\text{CCl}_4$  solution of pure crepe rubber at 80 to 90° until the evolution of  $\text{HCl}$  ceases. The commercial viscosity grades are determined for a 20 per cent solution in toluene at 25°, and consist of 1000, 125, 20, 10, and 5 centipoise viscosities. The specific gravity of chlorinated rubber is about 1.64, nearly twice that of the natural rubber. Manufacturers of the materials generally recommend the 125 cps grade for adhesive use. The viscosity-concentration curves of chlorinated rubber in toluene are shown in Figure 28<sup>189</sup>. Rubber adhesives with high initial tack and permanent flexibility are obtained by degrading the rubber with a mild acid or steam, followed by chlorination in solution<sup>189a</sup>.

One of the first adhesives prepared from chlorinated rubber was Peachey's<sup>188</sup>; at the same time he discussed the chlorination of rubber in carbon tetrachloride solution. Ellis also prepared a number of chlorinated rubber adhesives, in one instance dissolving the material in carbon bisulfide and employing it to bond wood and leather<sup>190</sup> and in another case dissolving the material in  $\text{CCl}_4$  or naphtha for use as an adhesive<sup>191</sup>. Solutions of chlorinated rubber in organic solvents are specially mentioned as adhesives for waxed paper<sup>192</sup>.

Chlorinated rubber is compatible in most plasticizers and in a large number of drying oils. It may in fact be dissolved in tricresyl phosphate, dimethyl phthalate, and butyl stearate after warming to a temperature of 100°. Chlorinated diphenyls are frequently employed as plasticizers for the chlorinated rubber. The manufacturer of chlorinated rubber recommends the following proportions for different adhesives prepared from chlorinated rubber<sup>189</sup>.

#### Non-drying adhesive.

Chlorinated rubber (1000 cps)	parts 2
Plasticizer	1.5-3
Drying adhesive.	
Chlorinated rubber (20 or 125 cps)	2
Plasticizer	0.5 to 1.0
Resin	1.0 to 3.0

A number of chlorinated rubber adhesives have been patented by Tomiscek, Dodge, and Calva, who specified chlorinated rubber 2 to 17 per cent, resins 40 to 80 per cent, plasticizers 1 to 20 per cent, and waxes 1 to 30 per cent<sup>193</sup>; resins specifically mentioned were dammar gum, ester gum, and polymerized terpenes. Baxter and Moore examined the properties

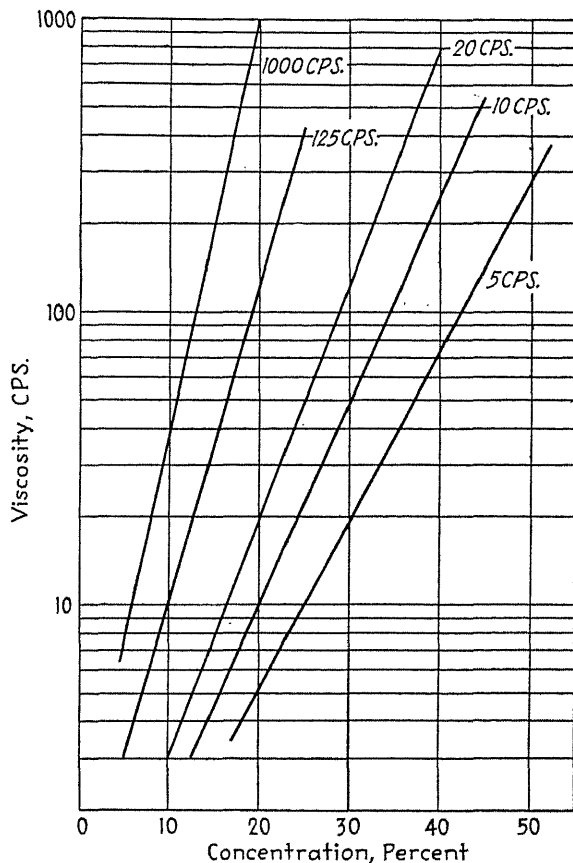


Figure 28. Viscosity-concentration curves of different grades of chlorinated rubber at 25°C.

and uses of chlorinated rubber, establishing some relationship between viscosity and the degree of chlorination. They also pointed out that heating carbon tetrachloride solutions of chlorinated rubber for several hours greatly reduced the viscosity<sup>194</sup>.

Chlorinated rubber adhesives have also been specified for various tapes<sup>195</sup>; castor oil and dibutyl phthalate were employed as plasticizers. Aside

from chlorinated rubber, brominated rubber adhesives have been prepared by Warner, who described a partial bromination<sup>196</sup> of the rubber. Trumbull discussed chlorinating a rubber surface and adhering a plasticized polyvinyl chloride thereto<sup>197</sup>. Solutions of chlorinated natural rubber are employed as cements for rubber to metal, particularly natural rubber containing a certain proportion of synthetic rubber<sup>198</sup>. Phillips made an extensive review of chlorinated rubber patents in the United States and other countries<sup>199</sup>.

Gordon prepared a waterproof adhesive and sealing compound employing calcium sulfate, portland cement, chlorinated diphenyl, and chlorinated rubber as a binder<sup>200</sup>. Beta-pinene polymers with a melting point of 80 to 150° are described as good tackifiers for chlorinated rubber or rubber hydrochloride adhesives<sup>201</sup>. These are recommended for bonding miscellaneous materials together. An anhydrous rubber cement was prepared by Raynolds by chlorinating the rubber to a minimum of 65 per cent chlorine and removing nitrogenous impurities from the solution with absorbent carbon. The chlorinated rubber was recovered by precipitating it from carbon tetrachloride with methyl alcohol<sup>202</sup>. Chlorinated rubber hydrochloride has also been prepared<sup>203</sup>. A foundry core binder has been prepared from a combination of chlorinated rubber and chlorinated paraffin wax<sup>203a</sup>.

Chlorinated rubber emulsions have also figured prominently in the technical literature. McDonald prepared an adhesive by polymerizing chloroprene in a solvent which was then emulsified with water and chlorinated rubber as an emulsifying agent<sup>204</sup>. Little prepared a chlorinated rubber emulsion in the presence of a glycol ester of a rosin acid (with a melting point of 23° to 70°)<sup>205</sup>.

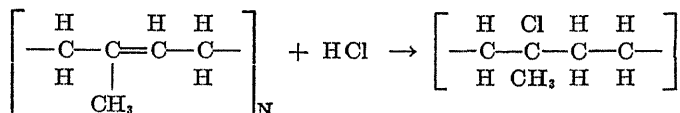
Chlorinated rubber has proved suitable for bonding various types of rubbers and in bonding metal to rubber. The general technique of application is to clean thoroughly the surfaces to be joined and to apply a film of chlorinated rubber suitably plasticized (with chlorinated plasticizers for maximum chemical resistance). When the solvent has partially evaporated and the film has become slightly tacky, the surfaces may be pressed together, if the assembly is a cold press job. Otherwise, complete removal of solvent is necessary for heat-welding. In dissolving the powdered chlorinated rubber in its solvent, it is added slowly and stirred vigorously to secure uniform solution. In the table which follows, various compatible and incompatible materials with chlorinated rubber are noted:

Compatible with Chlorinated Rubber  
Linseed oil (raw and boiled)  
Tung oil  
Soybean oil  
Dammar gum

Incompatible with Chlorinated Rubber  
Polystyrene  
Natural rubber  
Cyclized rubber  
Gilsonite

Compatible with Chlorinated Rubber	Incompatible with Chlorinated Rubber
Coumarone-indene resins	Polychloroprene
Rosin	Urea-formaldehyde
Dipentene-maleic anhydride "adducts"	Shellac
Oil-modified phenol-formaldehyde	Cellulose esters
Modified glyceryl phthalate	Polyvinyl chloride-acetate
Hydrogenated methyl abietate	Olefin polysulfides
"Vinsol"	
Chlorinated diphenyls	

Rubber hydrochloride is known less as a proprietary adhesive than as a thin, transparent packaging material fulfilling many important roles because of its good stretchability and imperviousness to moisture. Much of the art developed for rubber hydrochloride in the field of adhesives was in the bonding of thin layers of film to make an air-tight package. As in the case of chlorinated rubber, rubber hydrochloride originated in the latter part of the nineteenth century, though commercial application occurred at a more recent date. The formation of rubber hydrochloride is generally accepted as an addition reaction of hydrochloric acid and the isoprene units of natural rubber in the following manner<sup>206</sup>:



#### *Rubber Hydrochlorides*

Gaseous anhydrous HCl is added to solutions of rubber at low temperature to effect the formation of the new polymer. The rubber hydrochloride is washed free of excess HCl. Above 145° it decomposes rather easily and loses HCl. It is generally soluble in aromatics and chlorinated hydrocarbons, though insoluble in ethers, esters, and alcohols; it is known to the trade as "Pliofilm".

The origin of rubber hydrochloride may be followed through the researches of the effect of halogen acids upon rubber. Harries, for example, prepared a hydrogen bromide rubber product<sup>207</sup>, obtaining a material which did not resemble rubber which was soluble in chloroform. Soll and Koch prepared a rubber derivative by treating a benzene solution of rubber with hydrofluoric acid and warming for a number of days. The reaction was expedited by heating the solution in an autoclave at 100° for 16 hours<sup>208</sup>. They mentioned the use of the solutions of rubber hydrofluoride as adhesives.

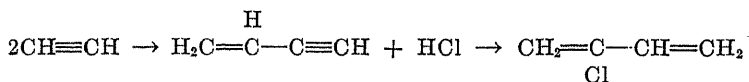
Winkelmann did a thorough job in preparing a number of adhesives employing rubber hydrochloride as a base material<sup>209</sup>. In one case, he combined the rubber hydrochloride with chlorinated paraffin, and a coumarone-indene resin as tackifying agent. Ester gum was utilized in

other examples; sulfur and coumarone-indene resins were used in still further adhesive formulations. A vulcanizable adhesive composition has also been prepared by Winkelmann and Moffett from 20 to 80 parts of sulfur to 100 parts of rubber hydrochloride<sup>210</sup>. A permanently tacky adhesive was formulated with rubber hydrochloride by milling rubber hydrochloride with 1 to 3 times its weight of hydrogenated methyl abietate or an aryl or alkyl ester of a resin acid<sup>211</sup>. It was specifically described as a good adhesive for rubber. Neoprene bonded to various metals was made possible by adhesives prepared from halogenated rubber derivatives and vulcanizing agents, according to Winkelmann<sup>212</sup>.

Some of the art of preparing moisture-proof bags of rubber hydrochloride is described by Brown and Snyder<sup>213</sup>. Because the films of rubber hydrochloride are quite readily stretched and easily fitted over odd-shaped curvatures and because they have the necessary chemical resistance, they have been extensively employed for packaging miscellaneous foodstuffs. The rubber hydrochloride is readily heat-sealed to itself to make a permanent air-tight weld. Other vulcanizable adhesive compositions of halogenated rubber derivatives are suggested<sup>214</sup>. Laminates of rubber hydrochloride to paper for packaging purposes have been prepared<sup>215</sup>. Rubber hydrochloride films have been made by Snyder in which there was an excess of wax, so that on the evaporation of solvent, a coating of wax will remain on the surface<sup>216</sup>; this technique has been adapted to other adhesive problems. Vincent disclosed further problems of heat-sealing plies of rubber hydrochloride<sup>217</sup>. Latour plasticized rubber hydrochloride sheets with a small amount of dibutyl sebacate<sup>218</sup>. Grafton prepared rubber bonding compositions consisting of rubber hydrochloride and 1,3-dichloro-5,5-dimethyl hydantoin<sup>219</sup>.

### Polychloroprene Cements

Numerous adhesives have been made from polychloroprene (neoprene), enjoying wide usage in shoe manufacture, industrial rubber goods, and in the bonding of rubber to metal parts. The development of polychloroprene is due in a large measure to Nieuwland, who discovered the practical technique of converting acetylene to vinylacetylene with the aid of an ammoniacal cuprous chloride catalyst<sup>220</sup> and to Carothers, who converted the monovinylacetylene to chloroprene by reaction with hydrochloric acid<sup>221</sup>. The reaction may be represented in the following manner.



*Chloroprene*

Chloroprene polymerizes much more rapidly than butadiene, and if the polymerization is arrested when about one-third complete, the polymer resembles unvulcanized rubber, while when allowed to go to completion, it resembles vulcanized rubber. Emulsion polymers of chloroprene, for example Neoprene G, are widely used<sup>222</sup>. Small amounts of stabilizers such as phenyl-beta-naphthylamine are usually added after polymerization to prevent further cross-linking or cyclization, which would stiffen the polychloroprene during storage. Carothers and Collins described the commercial preparation of chloroprene<sup>223</sup> and Williams the method of polymerizing it<sup>224</sup>.

In preparing polychloroprene for use as an adhesive, McDonald milled sheets not thicker than 1/16 inch and subjected the material to the action of an alcohol solvent to remove any malodorants<sup>225</sup>. Wedger utilized the polychloroprenes as adhesives for the manufacture of shoes, employing a wood resin as a softener. Zinc oxide was used with vulcanizing ingredients in a solvent of benzene and trichloroethylene to form the adhesive composition<sup>226</sup>. Polymerized chloroprene dissolved in cyclic ethers of glycols have been recommended as an adhesive agent for bonding rubber, where it is desired that the chloroprene adhere to the rubber without any solvent attack upon the rubber<sup>227</sup>. Ethylene oxide, propylene oxide, isobutylene oxide, tetramethylene oxide (tetrahydrofurfurane), diethylene oxide and other solvents are mentioned. As a typical adhesive composition of a fluid, free-flowing character, 1 part of polymerized chloroprene is dissolved in 6 parts of propylene oxide. A typical application of this cement is the cover of a golf ball to the rubber thread-wound core. Polychloroprene and zinc and calcium resinate, dispersed in volatile solvent, form the basis of a useful adhesive<sup>227a</sup>.

In preparing the deodorized material for adhesives, the process of milling the polychloroprene in the presence of ethyl alcohol is described<sup>228</sup>. This is followed by reincorporating the stabilizer (phenyl-beta-naphthylamine 2 per cent). It is quite probable that as in the case of natural rubber, the prolonged milling into thin sections does invite the absorption of oxygen and the attainment of an improved adhesive due to some depolymerization, though the rate at which this occurs is less rapid in polychloroprene than in natural rubber.

Kronquest and Robison developed a stable chloroprene base composition for sealing can ends to their bodies. The addition of various plasticizing and filling ingredients modified the base material so that an emulsion could be readily produced. Polychloroprene, a gelled drying oil, alkyd resin, ester gum, and glue were suspended in an aqueous ammonium hydroxide solution to form the sealing material. Bentonite clay and diatomaceous earth were employed as fillers<sup>229</sup>. Diethylamine and mono-

ethanolamine were employed as stabilizers for polychloroprene adhesives in toluene, xylene, and carbon tetrachloride<sup>230</sup>.

Aqueous dispersions of polychloroprene, treated until free of malodorant by agitating with an aliphatic hydrocarbon solvent, were blended with wetting agents and soaps to prepare adhesive latex<sup>231</sup>. In applications of cementing outsoles to shoe bottoms, Wedger applied the polychloroprene adhesive film and allowed it to dry. When ready for assembly they were wetted with a suitable solvent such as benzene or xylene. Aniline-butyr-aldehyde served as a curing agent, and monoethanolamine and diethylamine were present to extend the pot life of the adhesive composition<sup>232</sup>. Liquid adhesives containing polychloroprene have a tendency to gel on storage and the presence of diethylamine and an ethanolamine will increase storage life<sup>233</sup>.

Yerzley studied the adhesion of neoprene to metals with the aid of a chlorinated rubber—polychloroprene cement<sup>234</sup>. While he observed the best results with newly prepared batches of polychloroprene, he found the most important factors in securing good adhesion to brass were the condition of the surface and its porosity. The value of brass plating in securing good adhesion has been reviewed<sup>235</sup>. McDonald attributes part of the efficacy of his adhesive compositions to the particular solvent combination he employs, reporting 1 part of polychloroprene to 2 parts of benzene and 3 parts of trichloroethylene to be his preferred practice<sup>236</sup>. Lower solution viscosity is also obtained by adding a small amount of alcohol. Wood rosin, magnesium oxide, and zinc oxide are milled into the polychloroprene in preparing it for adhesive use on shoe and leather products. A typical adhesive composition follows:

	parts
Polychloroprene	900
Magnesium oxide	90
Wood rosin (Type FF)	45
Zinc oxide	45
Phenyl-beta-naphthylamine	9
Benzene	1690
Trichloroethylene	2850
Sulfur	27
Aniline-butyr-aldehyde	12
(cond. product-accelerator)	

Polychloroprene dissolved in methyl propyl ketone or a dialkyl ketone containing at least 4 carbon atoms is specified by Browne in his composition<sup>237</sup>. The use of 1 to 5 per cent of the zinc chloride double salt of phenyl hydrazine, of the weight of polychloroprene<sup>238</sup> has been found to extend greatly the allowable open assembly period for the adhesive. This has been of great advantage in manufacturing operations for shoe parts

where time interval between the application of the adhesive and the assembly of shoe parts may be over night. It is claimed that this gain in open assembly time is accomplished without any loss in strength or effectiveness of the bonding agent.

Improvement in the stability of the polychloroprene cements by the addition of sodium thiosulfate during compounding has been pointed out<sup>239</sup>. Starkweather and Wagner state that up to 17 per cent concentrations are still usable after 5 months at room temperature. As may be expected, compounding with various vulcanizing agents tends to reduce the stability of the cement. A considerably higher ratio of solids content is possible with the polychloroprene cements than with the natural rubber solvent cements, though as already discussed, the latter is dependent upon the degree of milling and heating before dissolving in a solvent. There is very little gained by treating the polychloroprene beforehand in the same manner. Benzene, furan, toluene, carbon tetrachloride, ethylene dichloride, coal-tar naphtha, etc., are solvents for unvulcanized polychloroprene.

Blends of ketones or acetate with aliphatic hydrocarbons are recommended as solvents for neoprene cements<sup>239a</sup>. For example acetone and cyclohexane, heptane, or kerosene are suggested; or 30 volumes of methyl acetate to 70 volumes of high test gasoline. Good dissolution of neoprene, better storage, less toxicity and lower viscosity are claimed.

Browne prepared a mixed rubber-neoprene cement by dissolving rubber in gasoline and polychloroprene (neoprene) in butyl acetate and then combining the two solutions<sup>240</sup>. In applications to the manufacture of self-sealing fuel tanks for aircraft and in the production of barrage balloons, polychloroprene cements exceeded the requirements of the Army Air Corps specification No. 26571<sup>241</sup>. The adhesive film was tacky 3 to 15 hours and self-vulcanizing at room temperature. An improvement in the polychloroprene adhesives was noted by the addition of 1 to 10 per cent of ethylcellulose based on the weight of the former. The ethylcellulose may be either milled in with the other components or dissolved before addition<sup>242</sup>. Nugent assembled shoes having a lasting marginal portion of a polyvinyl resin coated with chlorinated rubber, which was secured with the aid of polychloroprene cement<sup>243</sup>.

In discussing the properties of polychloroprene cements, Earle points out that there is a greater amount of solid per area than the natural rubber types, and superior aging qualities<sup>244</sup>. This also means that greater penetration into porous surfaces is possible for the polychloroprene cements. Disadvantages cited are the lower initial strength and more expensive solvent requirements. However, polychloroprene adhesives age better and are more resistant to oils and greases than natural rubber.

Naunton briefly discussed the use of polychloroprene cements in bond-

ing to rubber surfaces and to metals<sup>245</sup>. One basic problem cited was the incompatibility of rubber and polychloroprene, which deterred developing high strength unless proper precoats were applied. No difficulty, it was pointed out, is encountered in bonding polychloroprene sheet to brass if some sulfur is present, though a precoat of chlorinated rubber is desirable in bonding polychloroprene to iron or steel, before vulcanizing the parts together. He also recommends an interlayer adhesive based upon a substantial proportion of rubber hydrochloride in combination with rubber and polychloroprene. The use of a butadiene copolymer synthetic rubber with proper vulcanizing ingredients is also recommended as a bonding agent for natural rubber to polychloroprene.

In the early stages of World War II considerable attention was given to polychloroprene cements because of the shortage of natural rubber<sup>246</sup>; there was a wide usage as a tank lining, for example. Earle prepared rubber-polychloroprene cements by dissolving the polychloroprene in an aromatic solvent and then adding a dispersed phase of rubber in petroleum distillate which was a non-solvent for the polychloroprene<sup>247</sup>. Earle also prepared polychloroprene adhesives by depolymerizing it partially during milling and plasticization. Among the plasticizers used were hexamethylene-ammonium-diethyldithiocarbamate ('Latac'), and diphenylguanidine, which in being nonvolatile at room temperature, remains in the film after spreading and retards the curing rate. However, if a small amount of a volatile amine such as morpholine is added as a volatile plasticizer, good solubility of the polychloroprene is realized and good adhesive properties are rapidly developed in use<sup>248</sup>.

Nimwegen employed polychloroprene and carbon black in the manufacture of bonded abrasive articles<sup>249</sup>, and in another example used Perbunan synthetic rubber as the bonding agent<sup>250</sup>. Polychloroprene reclaims as adhesives have been evaluated<sup>251</sup>. As another approach to the adhesive problem, Eustis and Orrill developed a composition containing incompletely polymerized chloroprene as a component<sup>252</sup>. A quick-curing polychloroprene cement was prepared by Bake, who compounded unvulcanized material up to 2 per cent of its weight with sulfur, and used it with an admixture of an accelerator of lead oxide and a butyraldehyde-amine resin<sup>253</sup>. In vulcanizing polychloroprene tread stocks to the decks of ships, Morris prepared the assembly in the following order: Upper layer of vulcanized polychloroprene tread stock, fabric insert, unvulcanized layer, polychloroprene cement, and then the deck<sup>254</sup>. Saunders and Morrison prepared a high strength adhesive by selecting either chloroprene or butadiene-acrylic-nitrile copolymer and dispersing the rubber in a continuous phase of thermosetting synthetic resin in solution<sup>255</sup>.

Also to be considered in the role of cements and impregnating agents are

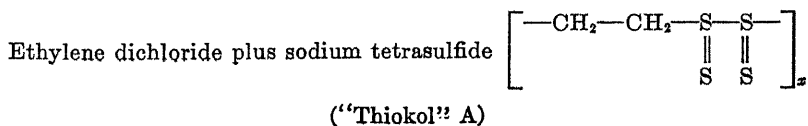
various types of polychloroprene latex. The particle size is smaller than the natural rubber latex and will more readily penetrate porous bodies such as cloth. One type of polychloroprene latex (neoprene 571) has been recommended for combination with various synthetic resins<sup>256</sup> exhibiting general versatility with many materials. Combinations with polyvinyl acetate, phenolic resins, alkyds, proteins, urea and melamine-formaldehyde types are described. By this technique properties may be varied at will, offering a new approach to the development of specialty adhesives. A small amount (1 to 10%) of polyvinyl acetate to a chloroprene adhesive, will impart high initial tack<sup>256a</sup>.

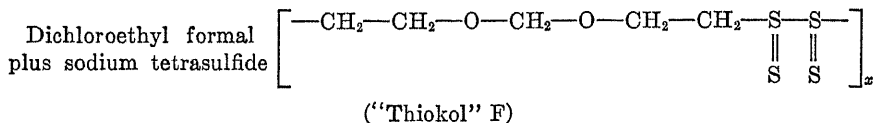
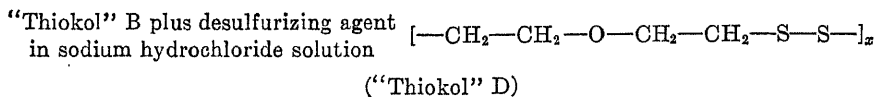
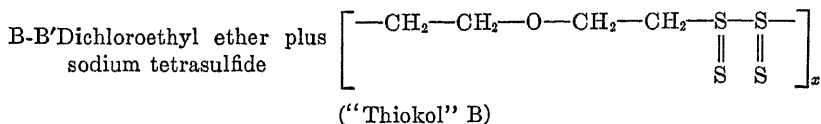
In the field of pressure-sensitive adhesives, no promising results have been obtained as yet with polychloroprene, with properties comparable to those of the crude rubber base. This is due in part to the fact that certain tackifying resins effective with crude or reclaimed rubber are unsatisfactory with various synthetic rubbers. Generally, however, the adhesive strength of polychloroprene adhesives is retained after long aging periods, though as compared with natural rubber, the storage life of the solvent cements is not as satisfactory.

### Olefin Polysulfide Cements

Adhesive formulations based on olefin polysulfides ("Thiokol") are not as extensively employed as other types of rubber-like materials, though there are some outstanding adhesive applications involving these materials. These applications are usually dependent upon the outstanding resistance offered by "Thiokol" to various aromatic fuels. Hence as sealing strips for gasoline tanks on aircraft and equivalent uses, where good chemical resistance at the glue line is desired as well as flexibility, these materials show much promise. However, the bonding of olefin polysulfides to metals and dissimilar materials is beset by many problems, as it is difficult to procure good, acceptable bonds of exceptional strength.

The development of the olefin polysulfides from the reaction of ethylene dichloride on sodium polysulfide is due largely to the efforts of Patrick, who first patented the materials in 1932<sup>257</sup>. While there was some previous work in preparing products of ethylene dichloride and sodium sulfide by Baer<sup>258</sup>, the commercial development took place with the polysulfide. There are a number of types of olefin polysulfides being manufactured today, employing variations in the starting materials, though following the general reaction of sodium tetrasulfide upon an alkyl group with chlorine at either end. The following examples are typical:





Improvements in freedom from odor and higher tensile strengths are characteristic with the latter types. The use of de-sulfurizing agents was a step in this direction<sup>258a</sup>. Compared with the other synthetic rubber-like materials, the olefin polysulfides are outstanding in chemical resistance, being unaffected by alcohols, ketones, and esters. Not requiring sulfur as a vulcanizing ingredient (zinc oxide is used), free sulfur is not extractable by gasoline, thus making this compound excellent for sealing gasoline tanks. Physical properties are not as high as those of other materials, with tensile strengths of only 1400 psi and elongations of 500 to 600 per cent. Decided creep under stress, particularly at slightly elevated temperatures is also exhibited by these products.

A highly important sulfur cement has been manufactured which carries in solution from 1 to 5 per cent of olefin polysulfide as a binding agent<sup>259</sup>. The olefin polysulfide rubber is cut into thin strips and added to the molten sulfur at 140 to 150° until dissolved. A concentrated batch containing 15 to 20 per cent of the rubber-like material is employed, though in practical use this is thinned with additional sulfur to permit about 5 per cent in the final mix. It may be blended with sand, the strongest composition being reported containing 4 parts of “Thiokol”, 36 parts of sulfur, and 60 parts of sand<sup>260</sup>. This cement is used for joining water pipes and tiles of acid pickling tanks.

Patrick prepared a number of adhesives from olefin polysulfides by condensing methylene compounds with sodium tetrasulfide, adding tetramethylthiuram disulfide to make a self-curing composition, and then dissolving in an organic solvent<sup>261</sup>. In dispersing “Thiokol” into a cement, the coagulated polymer is sheeted into thin strips and added to a suitable masticator. If uncured, carbon disulphide is preferred as the solvent, though if cured 1,1,2 trichloroethane is used as a solvent. A peptizing agent such as tetramethyl thiuram disulphide will aid solubility of the polymer. Five pounds of polymer per gallon may be obtained. Eger

employed a non-curing rubber cement for bonding the polysulfide rubbers<sup>262</sup>. Aqueous suspensions of olefin polysulfides have been employed as adhesives. In this example the product was further refined by conducting the reaction in the presence of a small amount of ethyl chloride which would substitute at one bond only<sup>263</sup>. Applications of heat and pressure aided the cure and assembly of articles bonded with olefin polysulfides<sup>264</sup>.

Applications of "Thiokol" sealing tapes, leaving a thickness of 0.015 inch when the fabric backing is removed, appear in fuselage seams and leakproof gasoline tanks. Such uses were quite extensive during the war<sup>265</sup>. More than 2 million feet of this tape had been used every month. An adhesive agent was prepared from B-B'-dichloroethyl ether in trichloroethane solvent<sup>266</sup>. Tetramethylthiuramdisulfide served as accelerator and dispersing agent (0.5 to 0.1 per cent).

### Miscellaneous Synthetic Rubber Cements

Numerous adhesive developments have appeared from the synthetic rubbers manufactured from butadiene. While their role in the adhesive field had not been prominent until the start of the second World War and the development of the tremendous synthetic rubber program, they give every indication of assuming an increasingly important position as adhesives. Partially polymerized butadiene (prepared in the manufacture of Buna 85 or 115) have been used as adhesives, the polymerization being stopped before the solid polymers are formed<sup>267</sup>. Ebert, Fries, and Garbsch report the polymerization of butadiene in the presence of sodium and a small amount of ethylene dichloride yield compounds with good adhesive characteristics<sup>268</sup>. Synthetic rubbers, particularly methyl rubber (dimethylbutadiene polymer), are cited as cementing agents for linoleum<sup>269</sup>. Phenolic or urea-formaldehyde resin adhesives are mentioned as bonding agents for the synthetic rubbers prepared from butadiene<sup>270</sup>. Chlorinated solvents such as ethylene dichloride or carbon tetrachloride and a small amount of ortho, meta, or tetraboric acid is generally added to the adhesive formulation.

Workability and solubility of rubber-like polymerizates of butadiene are improved by the addition of small amounts of asymmetric derivatives of hydrazine (phenylhydrazine, nitrophenylhydrazine, amino-phenylhydrazine). As little as 0.1 per cent suffices, and is added to the rolls during milling or during emulsion polymerization. The polymerizates become more plastic and the masticating action is improved. Buna S (styrene-butadiene copolymer) and Buna N (20 per cent acrylonitrile and 80 per cent butadiene) are rendered soluble in benzene by addition of 1 per cent of phenylhydrazine<sup>271</sup>.

In bonding a butadiene copolymer to a layer of fabric treated with rubber

latex and proteinaceous material, the addition of quinoline to the butadiene copolymer or to the intermediate bonding layer is reported to aid the adhesion considerably<sup>272</sup>. Bachle has prepared strong adhesives for paper and leather from two components: (a) non-sticky films of butadiene acrylonitrile copolymers and (b) strongly adhesive materials such as polyisobutylene and polyvinyl ethers<sup>273</sup>. In bonding to smooth metal surfaces, the use of finely powdered zinc and iron oxide in primer coats, before butadiene-acrylonitrile, has been examined<sup>273a</sup>.

Sarbrach discussed at length the technique and art of preparing adhesives from butadiene-acrylonitrile copolymers ("Hycar" OR-15 and "Hycar" OR-25). The excellent oil resistance of these synthetic rubbers

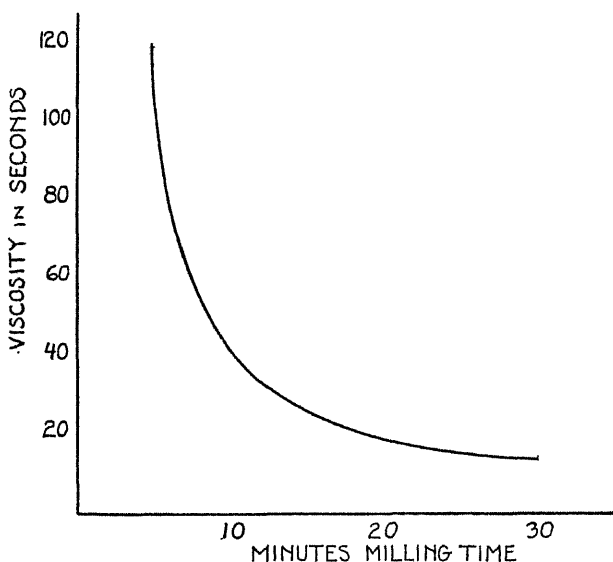


Figure 29. Effect of milling time on solution viscosity of *Hycar* OR-15, 15 per cent in chlorobenzene. (Sarbrach)

is retained by the adhesive films prepared from them. Vulcanized and unvulcanized butadiene copolymers are bonded to a wide assortment of materials such as leather, wood, glass, iron, steel, copper, aluminum, etc., which have been primed with chlorinated rubber or certain phenolic resins<sup>274</sup>. The effect of prolonged milling upon the butadiene acrylonitrile copolymer is shown in Figure 29; the solubility improves greatly. The viscosity was arbitrarily measured by Sarbrach as the time in seconds to flow from a 25-ml pipette. The temperatures under 70° were recommended on the milling rolls for best results. Data were also presented to show that the most stable cements from the standpoint of gelling upon storage were those prepared with frequent cutting back and forth of the batch during

breakdown to insure uniform blending of material. Another variable explored was the effect of time lapse between the preparation of the stock and mixing it into a cement with the solvents; it was noted that the sooner the batch was made into cement, the more stable the cement. For example, with a time lapse of 1.5 hours, the gelling time for a 10 per cent solution in chlorobenzene was 25 days; a lapse of 24 hours resulted in a gelling time of 14 days; and a time lapse of 7 days yielded a cement which gelled in 5 days. In general, the higher the initial viscosity, the shorter the shelf life. The best concentrations for synthetic rubber adhesive purposes appear to be between 15 to 20 per cent solids. Among the most effective solvents reported by Sarbrach are: ethylene dichloride, trichloroethane, chlorobenzene, butyl acetate, methyl ethyl ketone, nitropropanes and 1-chloro-1-nitroethane; one-third nitropropane and two-thirds toluene, ("Solvesso"), or methyl ethyl ketone have been observed to produce the most stable cements.

In compounding these butadiene copolymer cements, there are a number of low-temperature curing accelerators, which are particularly useful in fabricating balloons, fuel cells, and gas masks. Among the combinations are the following:

sulfur	1.5-2	parts	per	100	rubber
butyl eight	3-4	"	"	"	"
sulfur	2.0	"	"	"	"
zinc butyl xanthate	1.5	"	"	"	"
sulfur	2.0	"	"	"	"
2-mercaptobenzothiazole	2	"	"	"	"
butyraldehyde aniline	0.5-1.0	"	"	"	"

In application to the cement compositions at least part of the accelerator must be withheld until the adhesive is to be applied. Various stabilizers, such as benzoic acid or tartaric acid, were mentioned as prolonging the life of these adhesives. The butadiene acrylonitrile copolymers also blend well with chlorinated rubber (125 cps) which exerts a stabilizing action and enhances the adhesion. An important tackifier, produced by Germany during the war, has been particularly adapted to GR-S products. It is prepared from a tertiary butyl-phenol acetylene condensation product.

Henderson developed tacky rubber compositions by adding 20 to 50 parts of coal tar to a copolymer produced from an emulsion polymerization of 55 parts of butadiene with 45 parts of acrylonitrile<sup>275</sup>. Gelatin-glycerin composition was bonded to structural metal by an air-curing adhesive material formulated from an organic diisocyanate or butadiene copolymer rubber<sup>276</sup>. A liquid adhesive was prepared by Teppema and

Table 16. Qualitative Rating of Synthetic Rubber Adhesives—by Wehmer

Material	Tensile Before Aging		Strength After Aging		Viscosity Stability		Temperature Resistance		Application Characteristics		Tack Retention	
	good	excellent	good	excellent	good	fair	fair	excellent	good	fair	good	good
Reclaimed Rubber-rosin	good	excellent	good	excellent	good	fair	fair	excellent	good	fair	good	good
GR-M(Neoprene GN)	good	excellent	good	excellent	good	fair	fair	excellent	good	fair	good	good
GR-S (Buna S)	good	excellent	good	excellent	good	fair	fair	excellent	good	fair	good	good
GR-I (Butyl)	fair	fair	fair	fair	fair	fair	poor	poor	fair	fair	fair	fair
Thiokol	poor	poor	poor	poor	excellent	excellent	excellent	excellent	fair	fair	poor	poor

Manning by dissolving a copolymer of butadiene and acrylonitrile (25 per cent), with a copolymer of polyvinyl chloride-acetate. The ratio specified was 1 of the former component to 2 of the latter to a ratio of 2 to 1<sup>277</sup>. They also prepared a liquid adhesive with a ratio of 1 part of butadiene-acrylonitrile to 1 part of nitrocellulose. A cement has also been prepared from butadiene acrylonitrile and butyl formate solvent<sup>277a</sup>.

Wehmer prepared a chart with the qualitative ratings of a number of synthetic resin adhesives, which is reproduced in Table 16 on page 220.<sup>278</sup>

Of course, this only tells a part of the story, but it does indicate the trend toward synthetic resin adhesives and how they may be compared with natural rubber compositions. Just as synthetic resins in solution form have been employed as adhesives, synthetic resin dispersions have been used as substitutes for rubber latex. Jackson points out a number of applications to dipped goods, adhesives, and binding agents for granular materials<sup>279</sup>. As a group they are generally compatible with natural rubber latex. Butadiene polymers have been prepared as a latex in presence of emulsifier and polyvinyl alcohol<sup>280</sup>. Techniques have also been developed for concentrating synthetic rubber latices<sup>280a</sup>.

### Chlorinated and Cyclized Synthetic Rubber Cements

As could be expected, with greater quantities of synthetic rubber available than natural rubber, there has been considerable activity in the chlorination and cyclization of synthetic rubber has been considerable activity in the chlorination and cyclization of synthetic rubber and rubber-like materials. Several patents have been issued covering the chlorination of butadiene rubbers<sup>281</sup>. In order to obtain low viscosity grades suited to the lacquer and adhesives fields, the polymers were subjected to an oxidizing treatment at 80 to 140°. Butadiene-acrylonitrile copolymers have also been chlorinated to yield tough products, with properties closely dependent upon the degree of chlorination<sup>282</sup>. Chlorinated synthetic rubbers like the chlorinated natural rubbers show compatibility with drying oils. Endres described the characteristics of some of the chlorinated GR-S prepared in his laboratory<sup>283</sup>, claiming that the material is superior in mechanical properties to natural rubber. Most noteworthy is the improved flexibility, which should make these materials attractive as adhesives. Some of the properties of chlorinated GR-S described by Endres are as follows:

Chlorine content: 53%

Viscosity (20% in toluene): 0.50 to 20.0 poises

Solubility: Aromatic hydrocarbons, chlorinated hydrocarbons, ketones, and esters of organic acids

Stability: Equal to chlorinated rubber

Softening point: 75-80°

Specific gravity: 1.36-1.39

Adhesion: Equal to chlorinated natural rubber

Tensile strength: 5100 psi

Elongation: 18.7%

In addition to this chlorinated synthetic rubber, polychloroprene is also readily chlorinated to yield materials of potential interest to the adhesive field. The writer has observed in his laboratory that the best conditions for chlorinating polychloroprene appear to be at low temperatures in the presence of strong ultraviolet light and in a solution of carbon tetrachloride. Sixty-seven per cent chlorine content was obtained with this material. Chlorinated polychloroprene is much superior in chemical resistance to untreated polychloroprene.

Endres also described a number of cyclized synthetic rubbers<sup>282</sup>. In general higher temperatures (160 to 180°) are required for the cyclization of the butadiene-styrene copolymer (75 to 25 per cent). Chlorostannic acid and stannic chloride have been found effective as cyclizing agents. Films of the finished products appear to have very low vapor transmission, and show promise as a coating material. In general, considerably lower viscosity in solution is noted for cyclized synthetic rubbers as compared with cyclized natural rubbers. Endres does not report success in cyclizing polychloroprene.

There has been some mention of butadiene cyclized polymers employed as adhesives. The cyclization was carried out in contact with strong mineral acids<sup>284</sup>. Martin describes the reaction of conjugated butadiene polymers with  $\text{PCl}_5$  or  $\text{PBr}_5$ <sup>284a</sup>.

There has been considerable activity in recent years in bonding metal to metal and to other materials with the aid of rubber adhesives. While this subject will be covered more fully in a later chapter, a few of the fundamentals may be brought out at this time. For example, it is well known that the adhesion of rubber to metal is greatly enhanced by brass plating. Morron describes some of these processes<sup>285</sup>. Gross discovered a salt such as cobalt stearate which enhances metal-to-rubber adhesion<sup>286</sup>.

Various synthetic resins aid the cementing of rubber products. Knopp and Miedel employ phenol-formaldehyde and urea-formaldehyde as intermediate layers in the bonding of hard and soft rubbers<sup>287</sup>. Improved adhesion was noted by adding iron oxide to urea-formaldehyde. A heat-hardenable reaction product of a *m*-aryl diamine and formaldehyde with rubber latex has aided the bonding of rubber to fibrous materials<sup>288</sup>. Rubber dissolved in naphtha plus a partial polymer of divinylacetylene have yielded good adhesives for the bonding of rubber to metal, according to Humphrey<sup>289</sup>. In preparing latex adhesives, Wedger describes casein-formaldehyde condensation products deposited on the surfaces of the rubber particles to prevent premature coagulation<sup>290</sup>.

Among the recent applications of rubber adhesives of note are the "Cycleweld" process<sup>291</sup>, the "Meltbond" process<sup>292</sup>, and "Pliobond" adhesives<sup>293</sup>. The exact nature of these adhesives has not been disclosed as yet. Exceptionally high strengths are reported in bonding metal to metal and to metal and to other materials, with shear strengths at the glue line well over 2000 psi. Generally high temperatures (around 150°) are required to set these adhesives, though moderate pressure up to 250 psi may be employed at the time of bonding. The processes have lent themselves to the production assembly of important aircraft components. The high specific adhesion these rubber-base adhesives have for metal surfaces, such as aluminum, makes it possible to employ them in another manner, *i.e.*, primarily as a primer coating on the metal. When the coating is applied to a perfectly clean metal surface and properly cured, it serves as a film to which other low temperature-setting adhesives may be applied, such as the furan resin adhesives or the phenol-aldehyde types. These adhesives which do not of themselves have a high specific adhesion to metal will, however, bond to the strongly adhering film of rubber cement.

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## Chapter 9

### Adhesives from Cellulose Derivatives

Ever since the commercial development of cellulose nitrate, cellulose derivatives have taken a prominent position in the adhesives industry. Generally, tacky films are produced which are well suited to the bonding of miscellaneous types of materials such as paper, leather, and similar products. For example, it has been estimated that 61 million pairs of shoe soles were cemented to uppers by nitrocellulose adhesives in 1941.<sup>1</sup> The widespread use of sheets and molded products of cellulose derivatives also necessitates the development of assembly methods through processes of adhesion. The bonding of thermoplastic sheets entails the selection of proper solvent combinations to secure a correct balance of open assembly time and closed assembly time consistent with production requirements.

In the examination of the patent literature and the technical dissertations on the formation of cements from cellulose derivatives, one forms an early impression that much of the work has been conducted by trial and error. Numerous formulas have been proposed for cellulose ester adhesives, with various optimum proportions of solvents and plasticizers. With very few exceptions, little has been done to evaluate the influence of side groupings or the molecular weight distribution on the specific adhesion. We have already seen evidence in synthesizing synthetic resins that these are important influences. The manufacturing processes for cellulose derivatives commence with a naturally occurring material of high molecular weight, which through various esterification or etherification processes is converted to useful plastic materials. The solubility characteristics are to a great extent dependent upon the degree of substitution, on the average molecular weight, as reflected by the viscosity ratings, and on the nature of the solvent. The commercial grades of nitrocellulose, for example, and their comparative viscosity characteristics are given in Figure 30<sup>2</sup>. The nitrocellulose employed for this examination contained 11.8 to 12.2 per cent of nitrogen and the solvent comprised three parts of butyl acetate and 1 part of ethyl alcohol.

Kraemer determined the molecular weight distributions of cellulose and cellulose derivatives by the ultracentrifuge technique. Some of these data are reproduced in the table which follows<sup>3</sup>.

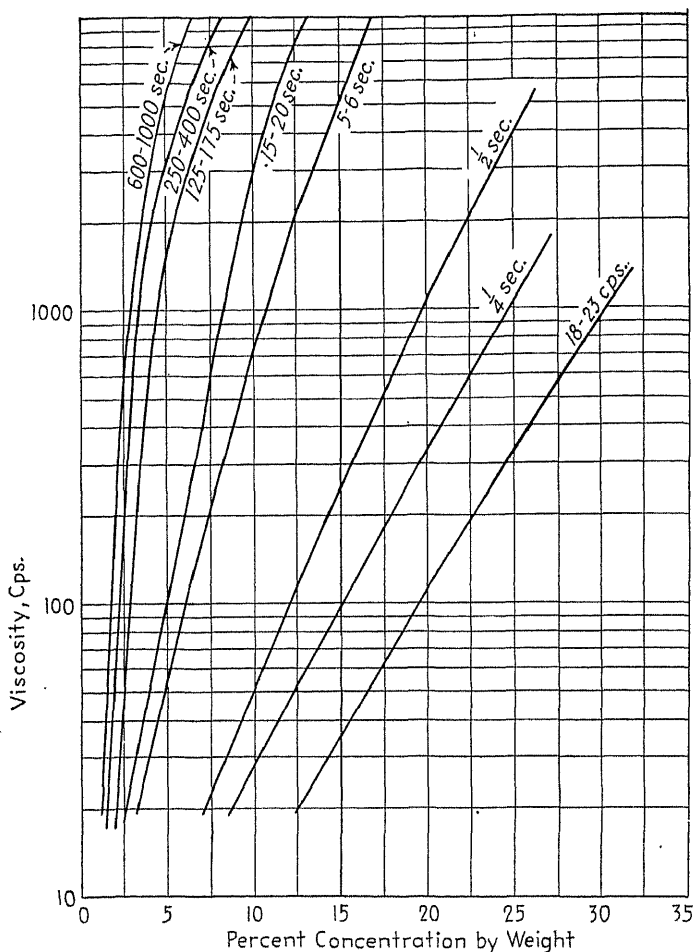


Figure 30. Viscosity-concentration characteristics of nitrocellulose solutions. (Data by Hercules Powder Co.)

#### Molecular Weight Determinations by Ultracentrifuge<sup>a</sup>.

Cellulose or Derivative	Molecular Weight	Degree of Polymerization
Native cellulose	Above 570,000	Above 3500
Purified cotton linters	150,000-500,000	1000-3000
Wood pulps	90,000-150,000	600-1000
Regenerated cellulose	30,000-90,000	200-600
Nitrocellulose (plastics)	125,000-150,000	500-600
Nitrocellulose ( $\frac{1}{2}$ sec.)	45,000	175
Commercial cellulose acetate	45,000-100,000	175-360

The type of nitrocellulose generally recommended for adhesive manufacture lies in the range of 11.8 to 12.3 per cent nitrogen. Kraus examined the solubility of nitrocellulose of differing nitrogen contents by covering a small sample with a specific amount of solvent and examining the solution after it had stood for 24 hours without stirring<sup>4</sup>.

Solubility of Nitrocelluloses of Varied Nitrogen Content (Kraus).

Solvent	Nitrogen Content (%)						
	10.36	10.65	11.06	11.53	11.86	12.45	12.71
Methyl alcohol	4	3	1	1	1	4	6
Ethyl alcohol	4	3	2	2	5	6	6
Methyl acetate	4	3	3	2	1	1	2
Ethyl acetate	4	4	3	2	1	1	2
n-butyl acetate	4	4	3	2	1	1	1
Ethyl lactate	3	2	1	1	1	1	1
Diacetone alcohol	3	2	1	1	1	1	1
Ethyl isobutyl ether	3	2	1	1	1	1	1
Dioxan	4	3	3	2	5	6	7
Acetone	4	2	1	1	1	1	1
Ethyl methyl ketone	3	2	2	1	1	1	1
Glacial acetic acid	3	1	1	1	1	1	4
Nitrobenzene	3	2	1	1	1	1	1

1. Clearly soluble	4. Very cloudy solution	6. Swollen
2. Almost clearly soluble	5. Extremely cloudy solution	7. Not affected
3. Slightly cloudy solution		

The solubility of other cellulose derivatives was examined in detail by Kline and Reinhart, who explored the four variables of plastic, plasticizer, solvent and diluent<sup>5</sup>. Commercial grades of cellulose acetate, cellulose triacetate, cellulose acetate butyrate, cellulose acetate propionate, cellulose ethers, chlorinated rubber, isobutyl methacrylate, and polymethyl methacrylate were among the film-forming materials included. From the standpoint of adhesion a qualitative indication of how readily the films which were formed and adhered to glass or cellophane provided the basis for selecting the adhesive. Films formed of cellulose acetate propionate and deposited from ketone or ester solvents appeared to have the best adhesion to such surfaces, though benzylcellulose films and isobutyl methacrylate resin films also showed strong tendencies in this direction.

The softening point and chemical resistance of cellulose derivative depend greatly on the degree of substitution as well as the chain length of the substituent. Malm and Hiatt pointed out that among cellulose esters those which contain side chains formed from fatty acid groups of 6 to 14 carbon atoms are eminently suitable for the rapid cementing of certain materials.<sup>6</sup> These esters soften and form an effective seal at approxi-

mately 100° under moderate pressure. The cellulose esters of less than 6 carbon atoms in the substituent are not as desirable due to considerably higher softening point; in the case of fatty acids of more than 14 carbon atoms, the film strength and bonding power are too low. Preference for cellulose caproate adhesive is indicated, which is substantially free from plasticizer and has a relatively sharp melting point. There is an absence of tackiness up to temperatures as high as 55 to 60°, permitting good storing qualities. The adhesive may be cast and stored in sheet form.

Relationships between the melting points of cellulose esters of different degrees of substitution were first reported by Sheppard and Newsome<sup>7</sup>; Malm and Hiatt confirmed these results. Tensile strength also falls off quite sharply as elongation increases under increasing length of substituent. Fordyce found that lower fatty acid esters of cellulose could be given good adhesive properties by oxidation processes<sup>8</sup>. He prepared an oxidized cellulose ester by oxidizing a partially hydrolyzed lower fatty acid ester of cellulose with a dilute aqueous solution of a water-soluble permanganate and 1 to 3 parts of sulfuric acid per 1 part of permanganate.

### Miscellaneous Adhesives from Cellulose Esters

In applications of sheets of "Celluloid," Hyatt required various cements to join them together and found that solvent cements worked quite satisfactorily<sup>9</sup>. While the details were not elaborated upon, it may be assumed that he followed the conventional procedure of liberally applying the solvent until the surfaces softened and then pressed the parts firmly together. Ellis prepared general utility cements from nitrocellulose, specifying a composition consisting of 10 lbs of nitrocellulose, 4 lbs of camphor, dissolved in 8 gallons of acetone, 1 gallon of amyl acetate, and 1 quart of creosote<sup>10</sup>. Cellulose nitrate received early attention in the manufacture of automobile safety glass, and was the first transparent plastic for this purpose. Wood first prepared safety glass in this country by coating a sheet of cellulose nitrate with Canadian balsam, and then placing it between two sheets of plate glass<sup>11</sup>. To Benedictus, however, goes credit for developing more practical techniques in the manufacture of safety glass from nitrocellulose sheet. He molded the transparent plastic between glass sheets with the aid of heat and pressure, rather than relying on cold setting<sup>12</sup>.

Rampichini developed a cellulose nitrate adhesive which exhibited excellent adhesion in the presence of organic acids. Twenty to 30 lbs, of "Celluloid" were added to 100 pounds of acetone together with a crystallizable organic acid such as oxalic acid ( $\frac{1}{2}$  to 2 lbs). The presence of the latter agent also increased the fluidity of the adhesive at the time of application<sup>13</sup>. Guiard also noted benefits from the addition of oxalic acid<sup>14</sup>.

About the time of Rampichini's development, a number of cellulose nitrate adhesives were prepared for the lamination of textile fabrics. Stoddard specified cellulose nitrate, amyl acetate, and blown castor oil or vegetable oil, applying the adhesive from some suitable rolls<sup>15</sup>. Arnold described a process of producing an artificial leather by applying a coating of cellulose nitrate adhesive to a fabric surface, followed by another face coating of cellulose nitrate. The latter could be embossed in a press with any desired decorative design<sup>16</sup>. See<sup>17</sup> prepared adhesives for fabrics from other cellulose esters, employing 60 parts of cellulose acetate, 20 parts of rubber, and 600 parts of ethylene dichloride.

Gum ammoniac and nitrocellulose dissolved in acetone functioned as a leather, wood, and rubber adhesive, according to Svensson<sup>18</sup>. Further developments in laminated safety glass were brought about by Bartelstone, who employed cellulose acetate or cellulose nitrate sheets and castor oil; the assemblies were united under heat and pressure<sup>19</sup>. Further developments in cellulose nitrate adhesives specified the inclusion of very finely divided fillers such as bronze powders, wood flour, gypsum, or asbestos mixed with the cement<sup>20</sup>. Plinatus employed finely divided cellulose nitrate containing a high boiling point solvent as an adhesive material<sup>21</sup>.

Modification of cellulose nitrate adhesives with synthetic resins was recognized as a step toward achieving high strength. Sheets of paper, cloth, brick, etc. were united, for example, with an adhesive based upon a cellulose derivative and the reaction product of a phenol and aliphatic ketone<sup>22</sup>. Still further combinations proposed as adhesives included cellulose derivatives and polyvinyl acetate, acid-catalyzed phenol-formaldehyde resin, or a diphenyl propane formaldehyde resin<sup>23</sup>. Thin films or sheets of material could be formed from these combinations. Cellulose esters or cellulose ethers in combination with polyvinyl acetate, which in itself is an excellent adhesive, were proposed again for adhesive purposes after depositing them from solvents<sup>24</sup>.

The manufacture of safety glass made new advances with the development of adhesives from cellulose nitrate and toluene-sulfonamide-formaldehyde resin combinations; camphor and tricresyl phosphate were used as plasticizers. Polyvinyl acetate and alkyd resin formulations with the cellulose nitrate were also suggested<sup>25</sup>. Adhesive surfaces have been developed upon sheets of cellulose nitrate or cellulose acetate by dipping them into plasticizers and attaching them to plate glass. This technique precludes the necessity of volatile solvents<sup>26</sup>. Dry adhesives were also manufactured from cellulose nitrate and ethylacetanilide, with a possible addition of polyvinyl acetate. In use, however, the surface was rendered adhesive by a suitable solvent<sup>27</sup>.

Cellulose nitrate adhesives have also been prepared in an aqueous emulsion form in the presence of water-soluble colloids such as polyvinyl alcohol, starch, urea-formaldehyde, or methylcellulose. Emulsification has been practiced with the plasticized cellulose nitrate dissolved in a water-insoluble organic solvent. For example, 20 parts of cellulose nitrate, 10 of butanol, 5 of resinous cyclohexanone product, 62 of ethylene glycol monobutyl ether, and 10 of tricresyl phosphate are emulsified in the presence of 95 parts of water, 5 parts of methylcellulose and 0.5 part of sodium mono- and dibutyl naphthalene sulfonate. Additional water may be added to this emulsified mixture<sup>28</sup>.

In bonding leather or wood veneer to iron or aluminum sheets, Menger employed cellulose nitrate adhesives, ethyl acetanilide, castor oil, and an asbestos filler<sup>29</sup>. Zangger described effective solvent combinations of alcohol, acetone, and amyl acetate in formulating a cellulose nitrate adhesive for wood and linoleum<sup>30</sup>.

In the manufacture of adhesive tapes, Schnitzler observed that a paper or cloth base employing a rubber cement on one side was unwound from a roll without offsetting by a layer of cellulose laureate on the other side<sup>31</sup>. It will be remembered that the higher cellulose esters do not acquire tackiness until heated to about 100°. Bernhard employed cellulose nitrate adhesives in the manufacture of bandages and surgical dressings, one composition comprising the following proportions<sup>32</sup>:

5-40% cellulose nitrate (5-480 sec. viscosity grade)  
1/3-10% gum benzoin and camphor  
0-20% zinc oxide  
40-80% acetone  
0-40% ethyl alcohol

The preparation of thermoplastic cements from cellulose nitrate or cellulose acetate in combination with a polybasic acid-polyhydric alcohol synthetic resin yielded strong, durable adhesives which could be heat-welded if necessary. Waterproofness, flexibility, and resistance to the action of oils and greases were characteristic of these materials. The surfaces to be bonded could be coated with this adhesive, and after the evaporation of the solvent stored until ready for use, and activated by heat<sup>33</sup>. Aryl sulfonamide formaldehyde<sup>34</sup> is mentioned as a modifier, in addition to the alkyd resin modified cellulose nitrate adhesive.

From a theoretical standpoint it is interesting to note that superior adhesive properties were exhibited by cellulose esters of heterogeneously linked dicarboxylic acids. For example, undissolved cellulose, which may be partially esterified or etherified, is reacted with phthalic anhydride in the presence of an organic tertiary base in molar proportions. Adhesives and materials suited to safety glass manufacture were prepared; cellulose

esters of dicarboxylic acids such as succinic acid, glutaric acid, thiodilactic acid, diglycollic acid, thiodiglycollic acid, etc. have also been described<sup>35</sup>. Malm and Fordyce prepared cellulose acetate diglycollate and cellulose diglycollate in the presence of pyridine, these esters showing good adhesion and being suitable for the laminating of glass, metals, woods, or fabrics<sup>36</sup>. Adhesives for cellulose triacetate and for cellulose acetate butyrate were prepared from condensation products of dicarboxylic acid ethers such as diglycollic acid and a polyhydric alcohol such as 1,3-butylene glycol<sup>37</sup>.

Alkylene oxides such as propylene oxide were observed to possess certain advantages as solvents for cellulose nitrate adhesives, and formulations were prepared in combination with ethyl alcohol and acetone<sup>38</sup>. Clark and Taylor evolved cellulose nitrate adhesives in contact with propylene oxide. For example, cellulose nitrate applied as an adhesive film was reactivated with 90 per cent propylene oxide and 10 per cent acetone or ester solvents. Another preparation mentioned was 99 per cent propylene oxide and 1 per cent dibutyl phthalate<sup>39</sup>. These particular solvents were exploited in the manufacture of shoes and other articles. For example, shoe parts were coated with a cellulose ester cement which was allowed to dry. Before assembly under pressure a softening solution was applied, which consisted of 40 per cent of  $\frac{1}{2}$ -sec. cellulose nitrate and 60 per cent of 18-sec. cellulose nitrate, the solvent being wholly or at least partly propylene oxide or isobutylene oxide. In other modifications of this technique, low-viscosity cellulose nitrate was applied first to secure penetration and good adhesion to the leather, followed in turn by a subsequent coating of high viscosity<sup>40</sup>. Pressure times for the assembly of the shoes was reduced to less than 10 minutes.

In a process for the manufacture of laminated safety glass, Watkins sprayed a mixture of dibutyl phthalate, monoethyl ether of diethylene glycol and nitrocellulose on the glass surfaces to be pressed together and interposed a transparent plastic to complete the assembly<sup>41</sup>. Heat and pressure were required in the final bonding. In the manufacture of adhesives for moisture-proofed cellophane (regenerated cellulose with a thin coating of cellulose nitrate), Snyder and Finzel prepared a composition with 5 to 30 parts of cellulose derivative, 5 to 30 parts of a synthetic resinous materials, 40 to 90 parts of ethyl lactate and alcohol or ether solvents in addition<sup>42</sup>. Edgar prepared a number of heat-energizable cements based upon cellulose nitrate and a compatible synthetic resin such as the alkyd resin type, which were suited to the bonding of regenerated cellulose and other non-porous materials<sup>43</sup>. A range of 0.6 to 2.0 parts of synthetic resin to 1 part of cellulose nitrate is preferred. The synthetic resins are prepared from polyhydric alcohol-polybasic acid condensation

products, preferably modified with ether alcohols and high molecular weight fatty acids. Due to absence of solvents, good bonds are claimed for glass and for metal surfaces.

Bjerg joined sheets of moisture-proofed cellophane with an adhesive containing a volatile solvent, plasticizer and a viscous oil. Dibutyl phthalate served as plasticizer with an oil selected from castor oil, corn oil or arachis oil<sup>44</sup>. Water-soluble glucose or cane sugar was treated with hydrochloric acid until a water-insoluble humus mass separated; after extracting with acetone, this was added to cellulose nitrate and plasticizer to prepare an adhesive material<sup>45</sup>. Rittman developed a workable adhesive for paper and cardboard by adding to 4 to 5 parts of cellulose nitrate, 1 part of plasticizer, 100 parts (by weight) of a mixture of solvents (40 per cent solvent for cellulose nitrate and 60 per cent non-solvent), and 5 parts of water tolerated by the second component in the solvent mixture<sup>46</sup>. Bennett reviewed the compositions of a number of cellulose ester adhesives<sup>47</sup>. He also mentioned ethyl crotonate as a solvent for both the cellulose nitrate and rubber. Typical compositions included:

cellulose nitrate	15	scrap nitrocellulose film	20
camphor	6	ethyl acetate	60
acetone	79	ethyl alcohol	20
filler	10	aluminum powder	10
cellulose nitrate	16	cellulose acetate	12
ethyl acetanilide	10	tricresyl phosphate	8
acetone	74	methyl alcohol	20
starch	15	ethyl acetate	30
		methyl acetate	30
		filler	25

Waterproof adhesives for cloth and leather have always been among the important applications of cellulose nitrate adhesives and the patent literature is replete with references to them. Under such circumstances we may find cellulose nitrate employed in combination with other materials. To mention a few, cellulose nitrate in an acetone solution of gum lac has been specified for this purpose; a reaction product of phenol and sulfur chloride has been combined with cellulose derivatives to form an adhesive<sup>48</sup>. Solvent combinations suited to bonding fabrics with cellulose nitrate were noted<sup>49</sup>. Dimethyl and diethyl esters of adipic acid were employed as cellulose derivative adhesives<sup>50</sup>. As a binder for waterproof sandpaper, Carlton employed 40 parts of a cellulose derivative, 3 parts of a resin, 1 part of camphor and 2 parts of a non-drying oil<sup>51</sup>. Ethers of water-soluble carbohydrates have been utilized in coating and adhesive compositions (for example, benzyl sucrose with 3 to 4 benzyl groups per mole of sucrose). With cellulose nitrate, tritoyl phosphate plasticizer, and solvent combina-

tions of benzene, toluene, and ethyl lactate, useful compositions are prepared<sup>52</sup>.

As an adhesive for joining moisture-proof regenerated cellulose, the following composition has been recommended (The ratio of resin to cellulose nitrate should not be less than 0.7 to 1.0)<sup>53</sup>.

Cellulose nitrate	15.7%
Gum dammar	15.0%
Monomethyl ether of ethylene glycol	30.4%
Ethyl lactate	16.8%
Ethanol	22.1%

Cellulose acetate and cellulose nitrate are united with a solvent cement based upon dimethyl phthalate, ethylene glycol monoethyl ether, and ethyl alcohol<sup>53</sup>. The flexibility of the adhesive layer may be controlled by adding not only plasticizers but also other thermoplastic synthetic resins. Polymerized vinyl resins fulfill this function in their relationship with cellulose nitrate adhesives<sup>54</sup>. Mono or dicyclohexyl phthalate has been specified as the plasticizer for nitrocellulose in adhesive layers<sup>55</sup>. Lacquer or adhesive layers formulated from nitrocellulose have their mechanical properties improved by the addition of small amounts of glycerol esters, according to Ernst and Kaufman<sup>56</sup>.

There has been some activity from time to time in the development of pressure-sensitive adhesive tapes employing cellulose nitrate adhesives, though the rubber derivatives discussed in the preceding chapter still are the more important materials in this article. Pendergast developed an adhesive tape which could be applied by pressure alone, and which could be unpeeled without the markoff characteristic of adhesive tapes. A large volume of castor oil was employed with cellulose nitrate in its manufacture, and the adhesive mixture dissolved in 25 per cent of butyl acetate, 10 per cent of butanol, 10 per cent of ethyl acetate, 5 per cent of ethyl alcohol and 50 per cent of toluene<sup>57</sup>. Tapes manufactured from cellulose acetate have been treated with a light application of solvent to convert at least a portion of it into an adhesive material. These were employed in shoe manufacture and pressed into contact with shoe soles, according to Newhall<sup>58</sup>. Pitman employed 7-sec. viscosity cellulose nitrate films and plasticizers which were activated with a solvent and pressed firmly to shoe soles<sup>59</sup>. Manufacturing techniques were also worked out for curing the cellulose nitrate adhesive layers under high radio frequencies. One process was specifically developed for the manufacture of shoes<sup>60</sup>. Under a frequency of 30 megacycles per second, the adhesive layer and leather surfaces adjacent to it were softened by heat generated within the material and the parts united. High frequency gluing techniques have been

developed particularly for the bonding of wood, and further discussions on this method appear in a later chapter.

Formamide has been suggested as a solvent for cellulose acetate-casein compositions. Other formamide-soluble materials such as dextrin or starch may be included in adhesive formulations<sup>61</sup>. Caprio and Walsh bonded cellulose acetate to other objects with the aid of alkyl phthalate plasticizers and no volatile solvents<sup>62</sup>. Cellulose acetate has also been adhesively united to colored prints with the aid of an adhesive of 60 parts plasticizer and 100 parts cellulose acetate. The addition of tannin extract from oak bark yielded some improvements in cellulose nitrate adhesives<sup>63</sup>. Roughening of leather was recommended for improved adhesion. Malm and Waring pointed out that water-soluble sodium or potassium salts of cellulose acetate phthalate or cellulose acetate succinate may be used in adhesive compositions<sup>64</sup>. King and Taylor added urea-formaldehyde condensation products to cellulose acetate compositions employed as adhesives, though the amount was small, ranging from 0.5 to 8 per cent based on the cellulose derivative<sup>65</sup>.

A thermoadhesive fabric prepared as a lining for collars and cuffs contained cellulose acetate with 60 per cent of ethyl-*o*-benzoyl benzoate. The adhesion remains intact during laundering of the articles<sup>66</sup>. Among other adhesives employed for uniting fabrics to form a stiffened article are cellulose acetate plus methylcellulose and dimethyl phthalate<sup>67</sup>. Other fabric adhesives proposed included cellulose acetate, triacetin, triphenyl phosphate and dimethyl glycol phthalate as plasticizers<sup>68</sup>. Fabrics and cellulosic materials have been coated with cellulose derivatives which have been emulsified with water. The proportion of the film-forming ingredient is at least  $\frac{1}{3}$  of the total—much more solids content than when the cellulose derivative is dissolved in a solvent by itself<sup>69</sup>. Waterproof, non-soiling, pressure-sensitive adhesive tapes were prepared by Thomas, who applied a waterproof coating of cellulose nitrate to a fabric base and an adhesive layer based upon rubber. Using about a 4-oz. fabric, he applied with a doctor knife a number of coats based upon the following composition<sup>70</sup>:

Coating Composition		Adhesive Layer	
Cellulose nitrate	12.6%	India rubber	8.1%
Ethyl alcohol	36.0%	Rosin	7.7%
Ethyl acetate	24.0%	Zinc oxide	12.1%
Ethylene glycol monoethyl ether phthalate	14.0%	Wool fat	12.1%
Lithopone	13.4%	Benzene	60.0%

Cellulose acetate (acetyl no. 51-54.5) is plasticized with 80 to 100 per cent of its weight with dimethyl phthalate as a safety glass interlayer<sup>71</sup>. As a general utility adhesive, Humphries prepared a composition based

upon 5 to 15 parts of glyceryl phthalate with a softening point of 60 to 95° and acid number of 50 to 90, plus 20 parts of cellulose acetate, 3 of plasticizer and 73 of solvent<sup>72</sup>. A cellulose nitrate adhesive possessing a quick initial set was prepared as an aqueous emulsion containing less than 25 per cent of water; 500 to 30,000-sec. viscosity nitrocellulose was employed in its manufacture<sup>73</sup>. Mixtures of cellulose derivatives or their solutions with condensation products of maleic anhydride and aliphatic alcohols formed the basis for adhesive layers employed in the manufacture of safety glass<sup>74</sup>. For adhering aluminum foil to cork compositions, an adhesive based upon cellulose nitrate, a soft glyceryl-phthalate resin, and 1 to 10 per cent of wax (calculated on total solids) has been utilized<sup>75</sup>. This is a heat-activated adhesive, and the presence of wax renders the deposited film non-adhesive at ordinary temperatures, so that the adhesive may be safely stored until ready for application at a temperature which will melt the wax. Among the waxes specified were carnauba wax, metallic stearates, and chlorinated paraffin wax.

Aside from its well known use as a paper and leather adhesive, cellulose derivatives such as the acetate have been applied to thin wood veneers which were subsequently woven together. Heat and pressure blended these into an attractive, durable assembly<sup>76</sup>. A German patent described a quick-hardening putty prepared from 30 grams of aluminum powder, 14 grams of cellulose nitrate, 21 cc of butyl acetate, and 35 cc of ethyl ether<sup>77</sup>. By replacing the cellulose nitrate with ethylcellulose and the butyl acetate with benzene, another variety of quick-setting putty was prepared. Von Artus points out, however, that the most important adhesives in the shoe industry are cellulose esters, and he states a typical formula involving 265 parts of cellulose nitrate, 450 of ethyl acetate, 300 of denatured alcohol, and 5 of castor oil<sup>78</sup>. Adhesives for the construction of airplane models were prepared by dissolving cellulose acetate in suitable solvents<sup>79</sup>.

A special adhesive was formulated to join cellulose nitrate sheet to hard rubber. This comprised 10 parts of cellulose nitrate to 10 parts of a crude tar, with solvent of acetate, ether and amyl acetate<sup>80</sup>. Cellulose derivatives applied as thin films were used to fill the interstices of glass fibrous webs, and to produce laminated assemblies. Cellulose nitrate, blown castor oil, and a plasticizer of butyl acetyl ricinoleate were specified for the adhesive<sup>81</sup>. A cement for bonding foils of cellulose acetate to textile fabrics was developed by Andersen. It utilized cellulose nitrate (11 per cent N) of 20- to 25-sec. viscosity, totalling 100 parts, methyl phthalyl ethyl glycolate 80 parts, acetone 335 parts, and monomethyl ether of ethylene glycol 540 parts<sup>82</sup>.

Malm and Clarke coated glass plates with a film of cellulose ester melted on to the surface and joined the coated faces to an interlayer of cellulose

ester. d'Andrea found cellulose nitrate adhesive useful in making lantern slides, combining the cellulose ester with a drying oil<sup>84</sup>. Increasing use has been made of mixed cellulose esters, such as cellulose acetate butyrate in the field of adhesives. Employing alkyl phthalate or dibutyl sebacate plasticizers, glass has been laminated with these cellulose derivatives<sup>85</sup>. Gourlay summed up the developments in nitrocellulose adhesives, pointing out that the cellulose ester, a resin, solvent, diluent, and plasticizer were present in most practical formulas. He outlined a number of the manufacturing processes in detail<sup>86</sup>. For higher solids content adhesives, the lower viscosity grades of cellulose esters are preferred, though for low cost, a motion picture film scrap has been widely specified in thermoplastic adhesives. *p*-Toluene sulfonamide formaldehyde resins are useful additions to cellulose acetate in the preparation of pressure-sensitive adhesives, though these as well as the phthalate plasticizers became less available during World War II due to material shortages<sup>87</sup>. In a novel application of cellulose plastic foil, Graton and Knight Company passed the foil of cellulose derivative through a solvent bath and then fed it continuously between two single plies of leather. When pressed between rubber pressure rolls, the parts were firmly cemented together and wound upon a drying drum while under normal belt tension. Belting for various drives was produced in this manner<sup>88</sup>.

### Solvents for the Cellulose Esters

An analysis of solvents for the cellulose esters is rather important to the formulation of adhesives from these materials. When solvents are used directly the surfaces are wetted and softened, and then firmly pressed together. Otherwise, the solvent cementing agent is flowed between joints snugly fitted together. A welding area rich in solvent is produced, which in the course of time diffuses through the body of the material, leaving a strongly cemented region, the substance of which is substantially the same as the balance of the material being cemented. Acetone and ethyl acetate are two typical solvent cementing agents.

On the other hand, the cementing of two chemically incompatible bodies does not result in a strong assembly, even though the solvent cementing agent is satisfactory for each material individually. For example, a cellulose acetate part may be readily welded to another cellulose acetate part through the medium of acetone; likewise a cellulose acetate-butyrate may be joined to cellulose acetate-butyrate. The use of acetone to cement cellulose acetate to cellulose acetate-butyrate does not produce a bond nearly as strong as it does for identical materials. Cellulose acetate and cellulose acetate-butyrate are chemically incompatible. This simple experiment, as well as other trials in bonding incompatible thermoplastics,

lends emphasis to the necessity of chemical compatibility in the cemented areas for the attainment of maximum strength.

Among those solvent characteristics which must be considered in the selection of a material for a cementing operation are the following: vapor pressure at temperature of application, molecular weight of solvent, comparative evaporation rate, boiling point of the pure material, the rate of diffusion through the solid material it is bonding, and its chemical compatibility with the material it is to bond. These characteristics are for the most part significant also to lacquer technology and the preparation of surface coatings for spraying or dipping. The rate of diffusion through the solid material is, however, important primarily in the use of solvents as adhesives for non-porous thermoplastic materials. After application, the rapidity with which the solvent diffuses through the thermoplastic will determine how rapidly the joint will reach its ultimate strength. Some of the physical constants of typical solvents for cellulose derivatives are enumerated in the accompanying table:

Physical Constants of Typical Solvents.

Solvent	Mol. Wt.	B.P. (C°)	Vapor Pressure at 30°	Rate of Diffusion* Through Cellulose		
				Nitrate	Acetate	Acetate Butyrate
				<i>mils per minute</i>	<i>mils per minute</i>	<i>mils per minute</i>
Methyl acetate	74.08	59-60	265 mm	—	3.0	—
Acetone	58.08	56.1	280 mm	5.0	3.0	4.0
Ethyl acetate	88.10	77.1	120 mm	2.3	0.75	2.3
Methyl ethyl ketone	72.10	79.6	119 mm	3.7	0.75	2.6
Ethyl alcohol	46.07	78.5	79 mm	0.25	NS†	NS
Butyl acetate	116.15	126.5	16 mm	1.0	NS	0.75
Amyl acetate	130.18	130-50	—	0.37	NS	0.75
"Cellosolve"	90.12	135	7 mm	0.37	NS	0.37

\* Rate of diffusion through solid sheets was obtained from the curves showing the loss of strength as a function of time of immersion in solvents, and represents the initial slope of this curve. See data by Delmonte<sup>99</sup>. Data for temperatures of approx. 25-30°.

† NS = Non-solvent.

Generally speaking, rapidly evaporating and rapidly diffusing solvents are sought for in cements for the cellulose derivatives, because they will permit the early development of high strength.

Bogin illustrates much useful data on the viscosity characteristics of nitrocellulose lacquers in different solvents<sup>90</sup>. In Figure 31, the effectiveness of toluene as a diluent is illustrated, with little or no change in viscosity up to 30 per cent of the solvent mixture in some cases. These lacquers

contained 12 grams of  $\frac{1}{4}$ -second nitrocellulose per 100 cc in volatiles. It will also be noted in these curves that the viscosity of the solutions increases with the boiling points and the molecular weight of the solvents.

The practical formulas developed for solutions of cellulose esters usually involve two or more solvents, as the combinations may prove more effective than a single solvent. This has already been pointed out for cellu-

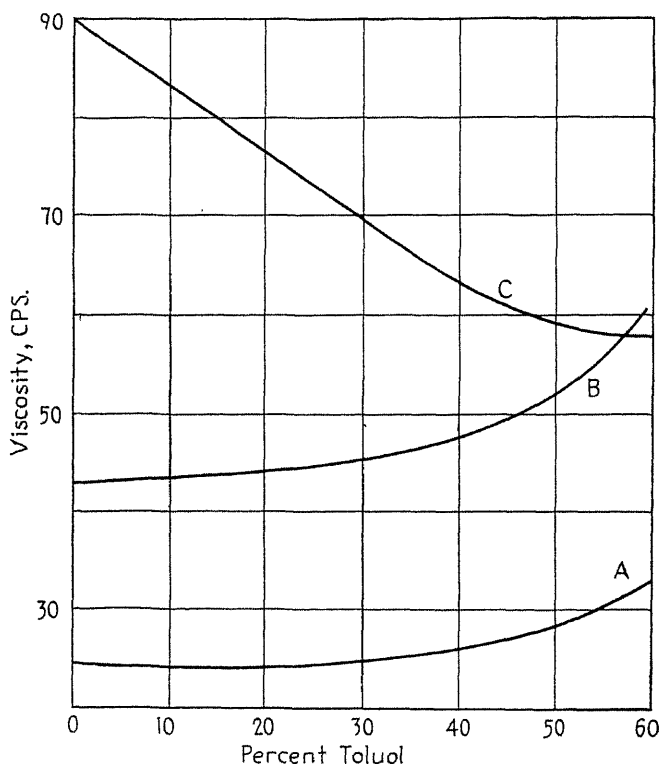


Figure 31. Effect of toluol on viscosity of nitrocellulose solutions. (Data by Bogin)

A. 80 per cent acetone—20 per cent ethyl alcohol.

B. 90 per cent *n* butyl acetate—20 per cent *n* butyl alcohol.

C. "Cellosolve".

lose nitrate, where the combination of an ester, alcohol, and toluene yielded a solvent combination which effectively dissolved the material, yet was low in cost because of the presence of adequate proportions of low-cost diluents. The problem, it is true, is more pressing for surface coatings where high surface losses are to be expected due to volatilization; nevertheless there are data which will prove useful to the development of adhesives. Extensive use of cellulose derivatives in the combined role of an impregnant and adhesive has already become apparent in the development of woven fabric laminates, where layers of cloth, treated with solutions of

cellulose derivatives are welded together into a high strength assembly. The fabric acts in the capacity of a reinforcing agent, as well as a component which will lessen the overall temperature sensitivity (change of physical properties with temperature) of the laminate. In new applications of this nature, it is advisable to refer to the experiences of others in doping fabrics with solutions of cellulose esters<sup>91</sup>. Kline and Reinhart point out that fabrics doped with cellulose acetopropionate and cellulose

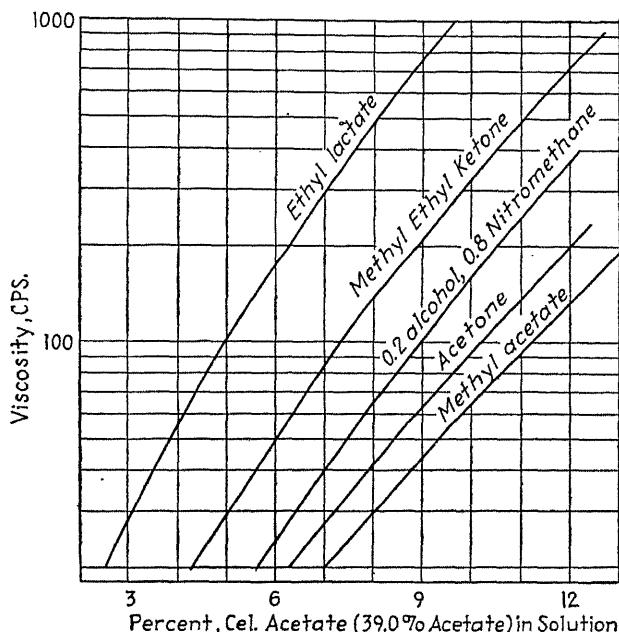


Figure 32. Viscosity-concentration characteristics of cellulose acetate solutions. (Data by Hercules Powder Co.)

acetobutyrate are fully equivalent to the more inflammable cellulose nitrate. The use of aryl phosphate plasticizers produces in general better initial tautness, and greater resistance to slackening in wet weather than other plasticizers examined.

There are a number of effective solvent combinations for cellulose acetate, which are suitable for use as solvent cements in bonding sheets of acetate together. These include such combinations as the following:

- 9 methylene chloride to 1 of ethanol
- 8 ethylene dichloride to 2 of ethanol
- 9 acetone to 1 of methanol
- 8 nitromethane to 2 of ethanol

The effect of various solvents on the viscosity of cellulose acetate solutions is shown in Figure 32. A low-viscosity lacquer grade of solvent was em-

ployed with an acetyl content of 39.0 per cent. Solutions were tested at 25°<sup>92</sup>. Various diluents such as toluene may be tolerated by solvent combinations for cellulose acetate; nitromethane, particularly, and acetone will permit inclusion of large amounts of toluene.

The compatibility of cellulose acetate with plasticizers is not as good as for cellulose nitrate or cellulose acetate-butyrate. Fordyce and Meyer reported the maximum limits of compatibility of a number of plasticizers with cellulose acetate. Included in their summary were the following:<sup>93</sup>

Plasticizer	Maximum Compatibility		
	Parts Plasticizer per 100 parts Cellulose Acetate		
	40.5% Acetyl	38.5% Acetyl	37.5% Acetyl
Butyl phthalyl butyl glycolate	60	50	25
Camphor	30	30	30
Cyclohexyl- <i>p</i> -toluene sulfonamide	30	30	30
Diamyl phthalate	20	10	10
Dibutyl phthalate	30	20	20
Dibutyl sebacate	10	10	10
Diethyl phthalate	85	85	85
Dimethoxyethyl phthalate	100	100	100
Dimethyl phthalate	85	90	90
Ethyl phthalyl ethyl glycolate	100	100	100
Methyl phthalyl ethyl glycolate	100	100	100
<i>o</i> , <i>p</i> -toluene ethyl sulfonamide	100	100	100
Triacetin	95	100	100
Trieresyl phosphate	25	20	20
Triethylene glycol diacetate	100	95	95
Triphenyl phosphate	35	35	40

### Cellulose Ether Adhesives

Cellulose ethers have figured prominently in the development of miscellaneous thermoplastic adhesives. Lilienfeld contributed much to the early art of formulating cellulose ethers not only as adhesives but also as lacquer coatings<sup>94</sup>. Lorand has shown that the size, polarity, and uniformity of distribution of the substituent groups govern the degree of substitution at which good solubility in organic solvents is obtained<sup>95</sup>. The alkyl ethers of cellulose become increasingly soluble in organic solvents and compatible with other chemicals with an increase in degree of substitution, ethylcellulose showing a maximum solubility in mixtures of alcohols and hydrocarbons at a degree of substitution of 2.4 to 2.5. At this degree of substitution ethylcellulose exhibits its lowest softening point (See Figure 33)<sup>95</sup>. A correlation may be drawn between the physical properties and the degree of substitution, the lower values of tensile strength occurring for the ethers with the lower softening points.

Ethylcellulose sheets and molded parts are more readily heat-welded to one another than the more common cellulose esters. This feature permits stronger assemblies to be made with the aid of heat. The type of ethylcellulose enjoying widest use has a degree of substitution in the neighborhood of 2.4 ethoxyl groups per glucose residue, falling within the range of 46.8 to 48.5 per cent ethoxyl content.

Kauppi and Bass undertook an evaluation of various solvents for ethylcellulose<sup>96</sup>. By an analysis of the load-elongation properties of cast films they observed that the highest strength and flexibility are usually obtained

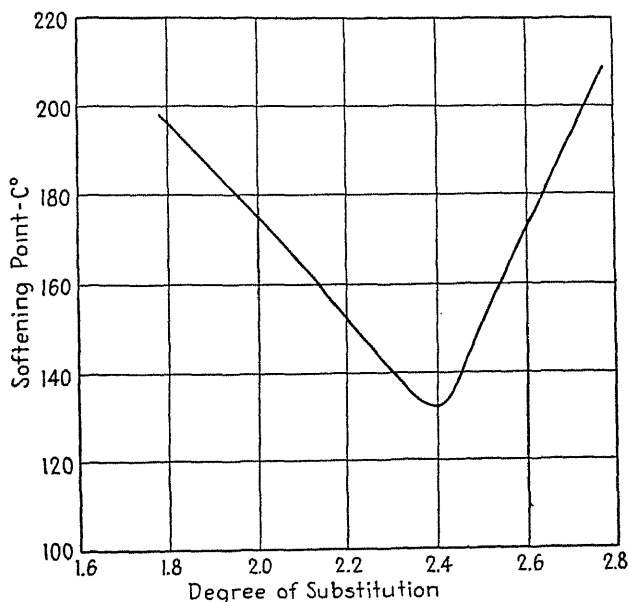


Figure 33. Relationship between degree of substitution and softening point of ethylcellulose. (Data by Lorand)

when the aromatic solvent is the last component to evaporate. Generally, when the methanol or ethanol component exceeds more than 40 per cent by volume of the mixture with toluene, the tensile strength and elongation of the films drop off rapidly. This behavior may be well taken into account in considering adhesion problems. In general, ethylcellulose films are inherently more flexible than those obtained from cellulose esters, possessing much greater elongation when comparisons are made in the absence of plasticizers.

While the best solvents for ethylcellulose are mixtures of 70 to 90 parts of coal-tar hydrocarbons (benzene, toluene, xylene, and high solvent naphtha) and 30 to 10 parts by volume of methanol, ethanol, or butanol, various

esters, chlorinated solvents, and ketones have excellent solvent action on the material. Care must be taken however, in sealing ethylcellulose sheeting to itself to avoid excessive use of a rapidly acting solvent if the sheet is too thin. In applying the solvent cement to the lapped edges of the thin sheets being joined, the adhesive flows in by capillary action and quickly seals. If heat is used to aid sealing, 110 to 125° is usually recommended. Various lacquer adhesives have been developed for sealing thin ethylcellulose sheeting to paper, cardboard, cloth, wood, leather, and metal surfaces.

Ethylcellulose solution viscosity is of course dependent upon the nature of the solvent and molecular weight. While ethylcellulose of more than 47.5 per cent ethoxyl content will dissolve in aromatic hydrocarbons, a marked lowering in solution viscosity is produced by the addition of an alcohol. Larger amounts of alcohol are required however, the lower the ethoxyl content in order to get solutions of maximum solids. Typical viscosities for 5 per cent ethylcellulose solutions are as follows at points of lowest viscosity:

	centipoises
70 toluene-30 butanol	140
70 toluene-30 isopropanol	125
70 toluene-30 absolute ethanol	96
70 toluene-30 methanol	70

In reviewing miscellaneous developments devoted to the formulation of adhesives from cellulose ethers, methylcellulose and sodium carboxymethylcellulose as well as ethylcellulose plays an important role. Methylcellulose is available commercially in a number of different viscosity types, including 15, 25, 50, 100, 400, and 1500 centipoises (2 per cent aqueous solutions at 20°). They are unique among the commercial cellulose ethers in that they are completely water-soluble. However, the water-solubility of other cellulose ethers has also been recognized as dependent upon the degree of substitution<sup>97</sup>.

Water-Solubility of Cellulose Ethers as a Function of Degree of Substitution.

Cellulose Ether	Alkali Cellulose (D.S.)
Methylcellulose	1.3-2.6
Ethylcellulose	0.8-1.3
Hydroxyethyl cellulose	1.5-2.5
Carboxymethyl (Na salt)	0.3-0.8

Water-soluble methylcellulose of uniform degree of substitution is attained through a proper balance in the system cellulose-NaOH-H<sub>2</sub><sup>98</sup>. Methylcellulose is best dissolved by first mixing with about  $\frac{1}{2}$  of the required water near boiling temperature (100°) and allowing it to soak for 20 to 30 minutes. The mixture is then cooled to room temperature after

the addition of the balance of cold water. These solutions are quite stable and not affected by changes in alkalinity or acidity from pH 2 to 12, though they may be coagulated from aqueous solution by saturated solutions of water-soluble salts of nitrates, sulfates, and chlorides.

Methylcellulose exhibits an interesting property significant to certain production applications of adhesives. Upon warming a solution of methylcellulose, the viscosity is lowered for a rise in temperature, then suddenly gels. By lowering the temperature, the gel can be returned to the original, smooth, flowable solution. The temperature at which the gelation occurs depends upon the concentration and the viscosity type of methylcellulose

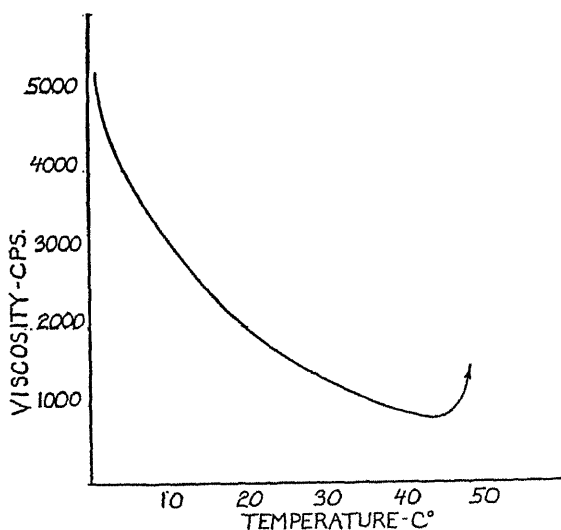


Figure 34. Viscosity-temperature characteristics of 5 per cent solution medium viscosity methylcellulose. (Data by Dow Chemical Co.)

The relationship between solution viscosity and temperature<sup>99</sup> is shown for a 50-cps. methylcellulose type in a 5 per cent aqueous solution (Figure 34).

Methylcellulose solutions will tolerate large proportions of polyhydric alcohols such as glycerol, diethylene glycol, sorbitol, etc. Small additions of the simpler aliphatic alcohols raises the gel point and increases the apparent viscosity. Aqueous solutions of methylcellulose may be readily blended with aqueous dispersions of starch, animal glue, dextrin, and water-dispersible natural gums, stabilizing the dispersions and improving the character of the adhesives obtained from these materials. In this capacity it also serves as a thickening agent for aqueous dispersions of adhesives. It has a wide use as a protective colloid for oil-in-water emulsions. Methyl-

cellulose adheres strongly to paper surfaces, rendering service as a grease-proof adhesive.

Methyl- and ethylcellulose adhesives, as well as lacquers and fibers have been known for some time, receiving early mention in patent literature<sup>100</sup>. Organic acid esters and cellulose ethers in combination with aryl sulfonamide formaldehyde resins have been suggested as possessing useful adhesive properties<sup>101</sup>. Ethylcellulose has also been described as a softening agent for phenol-formaldehyde resin binders, the combination being effected in a toluene-alcohol solvent combination, while methylcellulose is recommended for addition to water-soluble synthetic resins<sup>102</sup>.

Obst made a survey of the use of adhesives employing methylcellulose, finding their water-soluble properties to be of singular interest<sup>103</sup>. Liliensfield produced cellulose ether xanthates which showed promise as adhesives by first reacting upon sodium cellulose insufficient etherifying agents to produce an alkali-soluble derivative. Alkyl sulfates at 18 to 21° were used as the etherifying agent. In order to prepare it in solution form, more sodium hydroxide and carbon disulfide were added to dissolve the partially etherified cellulose<sup>104</sup>. Aqueous solutions of sulfonic acids of cellulose or starch ethers are used as adhesives. These are produced by reacting etherification products of cellulose with beta-hydroxyethane, alpha-sulfonic acid and others<sup>105</sup>. In other examples, cellulose ethers such as methylcellulose, are dissolved in water with sodium salts of sulfonic acids and employed as adhesives<sup>106</sup>. High adhesive power and resistance to micro-organisms is exhibited by some of these materials; they may be marketed as solids, but are readily dispersed in water.

Dry mixes or pastes have been prepared of starch and water-soluble salts of cellulose ether carboxylic acids. Sodium, potassium, and triethanolamine salts of cellulose benzyl or hydroxy benzyl ether carboxylic acid are mentioned<sup>107</sup>. Staudinger formed adhesives by reacting cellulose ether (2.5 per cent ethoxyl) with ethyl silicate and various high polymers of vinyl resins, all dissolved in a ketone solvent<sup>108</sup>. Alkali-soluble cellulose hydroxyalkyl ethers are specified for adhesives. They are prepared by reacting sodium cellulose at 5 to 10° with ethylene chlorhydrin or glycerol chlorhydrin<sup>109</sup>. Reaction of alkali cellulose with glycol-halogenhydrines produces water-soluble derivatives useful as adhesives or as thickening agents<sup>110</sup>.

In the manufacture of water-soluble alkyl cellulose, starch is added to the alkaline alkylating mixture when the cellulose is degraded. After neutralization the product is worked into a paste and it is proposed as an adhesive<sup>111</sup>. Mixture of aqueous solutions of cellulose ethers and aqueous emulsions of polyvinyl esters have shown some interesting properties and

potential applications as binding agents<sup>112</sup>. Water-soluble cellulose ethers from carboxylic acids are low in cost and stable in cementing power. Chloroacetic acid, chlorobutyric acid, and chloropropionic acid are reacted upon the sodium cellulose to produce these materials—sodium carboxymethyl cellulose. They are generally dissolved to the extent of 3 to 5 per cent in water (not more than 8 per cent), and are particularly applicable to such tasks as wallpaper hanging<sup>113</sup>. Methylcellulose, as applied as paper adhesive and coating, has been employed in conjunction with glue, casein, dextrin, and latex<sup>114</sup>.

Sichel proposed an aluminum salt of carboxymethyl cellulose as adhesive for pasting paper and wall paper<sup>115</sup>. Lilienfield was the first to propose alkali-soluble carboxymethyl cellulose as adhesives<sup>116</sup>; this has also been used for laminating non-fibrous sheets<sup>117</sup>. Gloor developed a coating of good adhesion to rigid surfaces comprising 2 to 10 per cent of methylcellulose, sodium silicate, and a water-soluble plasticizer such as glycerin, ethylene glycol, or glycerol-borate condensate<sup>118</sup>.

In commercial modifications of adhesives for envelopes, Davidson and Adams employed partially dextrinized starch (50 to 62 per cent), a fluidifying agent which renders the sugars inactive, and a water-soluble ether such as methylcellulose (3 to 10 per cent). Reaction was carried out at a higher temperature, and the final product dissolved in water and applied to the paper in an envelope machine<sup>119</sup>. Stringy fragments of water-soluble ethers have been used as binders for pencil or crayon rods<sup>120</sup>. Methyl cellulose adhesive applications on walls, book bindings, paper cartons, and the like have been considered as a starch substitute<sup>121</sup>. In other miscellaneous developments, ethylcellulose has been employed in conjunction with rubber adhesives<sup>122</sup>.

In evaluating methylcellulose as a pigment adhesive, a direct comparison with casein has been made. The cellulose ether was considered to have a more flexible coating and better resistance to ink penetration. The binder comprised 12 to 28 per cent of the pigment<sup>123</sup>.

Ethylcellulose has also fulfilled the role of a safety glass interlayer and adhesive. Glass plates have been laminated together experimentally with this thermoplastic material<sup>124</sup>. Plasticized with one of the rosin esters, ethylcellulose has proved useful as an adhesive in shoe manufacture<sup>125</sup>; it is compatible with a wide variety of plasticizers and other thermoplastic materials. When used in conjunction with nitrocellulose, high elongation as well as high tensile strength are imparted to the films. Kauppi prepared many of these combinations with a preferred range of 20 to 40 parts of nitrocellulose to 60 to 80 parts of ethylcellulose<sup>126</sup>.

The selection of plasticizers for ethylcellulose should be governed by

the fact that this unplasticized cellulose ether is inherently softer than the unplasticized cellulose nitrate or acetate and large proportions of plasticizers are not generally necessary. Castor oil, dibutyl phthalate, tricresyl phosphate, and triphenyl phosphate produce relatively soft, flexible films with ethylcellulose, while di (orthoxenyl) monophenyl phosphate and pentadichlorodiphenyl do not lower the yield point of ethylcellulose films as markedly. Chlorinated diphenyls are particularly useful as plasticizers for ethylcellulose adhesive formulations, being compatible in all proportions.

A very complete study has been made of ethyl cellulose-resin-plasticizer combinations, and while this study was developed largely for studying the usefulness of ethylcellulose as a coating material, much useful data was revealed on adhesive properties<sup>127</sup>. Fifty-six resins were selected for evaluation and examined in two combinations with ethylcellulose, and each proportion tested alone, with 10 per cent of dibutyl phthalate, and with 15 per cent of raw castor oil. Their adhesion to steel, copper, aluminum, tin plate, zinc, rubber, cellophane, wood, plaster, and glass surfaces were determined in most cases by cutting the film from the surface with a sharp blade held at an acute angle. Poorly adherent films could be stripped cleanly, fairly adhering films stuck in a few places, but strongly adhering films could not be cut from the surface in even tiny patches. A special technique was required however, for evaluating the adhesion to the thin films of cellophane. Some of the data reported in this survey by Hercules Powder Company are as follows<sup>127</sup>:

Formula	1	2	3	4	5	6
Ethylcellulose (low visc.)	10	10	10	10	10	10
Resin	5	5	5	10	10	10
Dibutyl phthalate		1.5			2	
Raw castor oil			2.25			3

With the above formulas, various resins were examined in combination with ethylcellulose and the adhesion of the resulting films to various specified surfaces was determined. The tests were entirely qualitative in action, though they show in an informative manner the effects of varying formulas. The great majority of films were cast from a solution comprising 80 per cent of toluene and 20 per cent of denatured ethyl alcohol, though for some of the natural resins a higher proportion of alcohols was required in the solvent mix. All surfaces were thoroughly cleaned before the films were applied. Typical results are:

	60% Rosin Ester 40% Phenolic						"Aroclor" 5460 Chlorinated Diphenyl					
	1	2	3	4	5	6	1	2	3	4	5	6
Formula No.	C	C	C	C	C	C	C	C	C	C	C	C
Compatibility	C	C	C	C	C	C	C	C	C	C	C	C
Adhesion to:												
Steel	F	G	G	P	G	G	F	P	P	F	P	P
Copper	G	G	G	G	G	G	P	P	P	P	P	P
Aluminum	F	P	P	F	F	F	G	P	P	G	P	P
Tin plate	G	G	P	G	G	G	G	P	P	G	P	P
Zinc	F	P	P	F	F	F	G	P	P	G	P	P
Rubber	P	P	P	P	P	P	P	P	P	P	P	P
Cellophane	G	G	P	Br	G	G	F	P	P	Br	F	P
Wood	P	P	P	G	F	P	P	P	P	G	P	P
Plaster	F	G	G	G	G	G	G	P	P	G	F	F
Glass	F	F	P	G	P	P	G	P	P	G	P	P
	"Beckacite 1100" Modified Phenolic						"Durez" 550 Pure Phenolic					
	1	2	3	4	5	6	1	2	3	4	5	6
Formula No.	C	C	C	C	C	C	C	C	C	C	C	C
Compatibility	C	C	C	C	C	C	C	C	C	C	C	C
Adhesion to:												
Steel	G	G	G	G	G	G	P	P	P	P	P	P
Copper	G	G	G	G	G	G	P	P	P	P	P	P
Aluminum	G	G	G	G	G	G	F	P	P	F	P	P
Tin plate	F	G	G	F	G	G	P	P	P	F	P	P
Zinc	G	G	G	G	G	G	F	P	P	F	P	P
Rubber	G	G	G	G	G	G	P	P	P	P	P	P
Cellophane	G	G	G	Br	Br	Br	G	G	P	Br	P	P
Wood	P	P	P	G	G	G	P	P	P	P	P	P
Plaster	P	F	F	G	G	G	P	P	P	P	P	P
Glass	G	G	G	G	G	G	F	P	P	F	F	P
	Ester Gum						Kauri Gum (Light Natural Resin)					
	1	2	3	4	5	6	1	2	3	4	5	6
Formula No.	C	C	C	C	C	C	C	C	C	C	C	C
Compatibility	C	C	C	C	C	C	C	C	C	C	C	C
Adhesion to:												
Steel	F	P	P	F	F	F	G	P	P	G	F	F
Copper	F	F	F	F	F	F	G	G	G	G	G	G
Aluminum	P	P	P	P	P	P	P	P	P	P	P	P
Tin plate	P	P	P	P	P	P	P	P	P	P	P	P
Zinc	F	P	P	F	P	P	G	G	G	G	G	G
Rubber	P	P	P	P	P	P	P	P	P	P	P	P
Cellophane	P	P	P	Br	Br	P	P	P	P	P	Br	Br
Wood	P	P	P	G	P	P	P	P	P	F	G	P
Plaster	G	F	P	G	G	G	P	P	P	F	G	G
Glass	F	F	F	F	F	F	P	G	F	G	G	G

Formula No. Compatibility	"Neville R-29" Coumarone-Indene Resin						"Petrex 1" Dipentene "Adduct" and Glycerol					
	1	2	3	4	5	6	1	2	3	4	5	6
Formula No.	C	C	C	C	C	C	C	C	C	C	C	C
Adhesion to:												
Steel	G	P	P	G	P	P	G	G	P	G	G	G
Copper	G	P	P	G	P	P	F	F	F	F	F	F
Aluminum	P	P	P	P	P	P	F	P	P	G	G	G
Tin plate	G	P	P	P	P	P	F	P	P	F	F	F
Zinc	P	P	P	P	P	P	G	G	G	G	G	G
Rubber	P	P	P	P	P	P	P	P	P	P	P	P
Cellophane	F	P	P	P	P	P	G	G	G	Br	Br	G
Wood	P	P	P	P	P	P	P	P	P	G	G	G
Plaster	F	P	P	P	P	P	G	G	G	G	G	G
Glass	F	P	P	P	P	P	G	G	G	F	F	F

F = Fair, P = Poor, G = Good, Br = Broken.

Polyvinyl acetate and polymethyl methacrylate, various alkyds, toluene sulfonamide formaldehyde resins, and some of the coumarone-indenes were not compatible and were not examined in the above tests, which are only a partial reproduction of the whole<sup>127</sup>. In general, however, good compatibility with a wide variety of resins is possessed by ethylcellulose. This compatibility includes a number of waxes, which assist in the preparation of hot-melt compositions without the benefit of solvent. In the bonding of thin films, as a matter of fact, ethylcellulose applied to one surface and a hard wax applied to the opposite surface have been employed as an effective seal and bonding medium; assembly was effected under heat and slight pressure<sup>128</sup>. Lovell and Russell prepared a shoe adhesive from ethylcellulose, gum dammar, toluene and acetone<sup>129</sup>.

### Sulfite Waste Liquors

Before concluding this chapter on adhesives of cellulosic origin, it appears desirable to examine some of the efforts in preparing adhesive materials from sulfite waste liquors obtained in the manufacture of paper. Large quantities of this material are available and it gives promise of yielding useful low-cost derivatives. It has already found extensive use as core sand binders in foundries. Tall oil and other materials processed from these liquors, notably the resin and fatty acids, should also serve as potential sources of adhesive materials. The tall oil produced in this country consists of 50 to 55 per cent resin acids, 30 to 45 per cent fatty acids, and 8 to 10 per cent unsaponifiables<sup>130</sup>. High yields of dehydroabietic acid are obtained from the resin acids.

Sulfite cellulose lye with its initial content of bases has been evaporated

to a specific gravity of 1.30 to 1.35 and employed as an adhesive without further treatment<sup>131</sup>. Sulfite waste liquors plus fatty oil pitches containing palmitic and oleic acids have been used as binders for highway roads<sup>132</sup>. Terra cotta clay plus solids of the waste sulfite liquor were adapted as a core sand binder for foundry use<sup>133</sup>. Linoleum cements have been prepared with clay dispersed in a waste sulfite liquor concentrated to 30°Bé. Casein solutions were also added to this combination<sup>134</sup>. Sulfite waste liquors for linoleum cements were also developed in Germany<sup>135</sup>. Conversion of at least a portion of the sulfite waste liquors by fermentation to convert the sugars to organic acids and evaporation to 50 to 60 per cent solids results in the formation of adhesive materials<sup>136</sup>. With the establishments of restrictions on rye grain or starch for linoleum cements or library pastes in Germany, recommendations were made for the use of sulfite waste liquors as substitute adhesives<sup>137</sup>.

Adhesives for paper or pasteboard were prepared by concentrating the sulfite liquors direct from the digester under vacuum at 60 to 70° to a specific gravity of 1.4. Sulfuric acid was added to avoid precipitation of the calcium salts<sup>138</sup>. A binder for fibrous substances was prepared by stirring concentrated sulfite waste liquors with albuminous substances to form a homogeneous mass at temperatures of 50 to 80°. Other synthetic resins were added directly to this mass<sup>139</sup>. Ritchie and Leach prepared water-soluble adhesives from waste sulfite liquors. They treated the material so as not to encourage fungus growths. The pH was adjusted to 7.0 to 7.3 and 5 to 20 per cent glycerol-ethylene glycol was added to maintain moisture. A fungicide such as sodium pentachlorophenate was also added<sup>140</sup>. The steps of neutralization, purification, and bleaching of waste sulfite liquors in the manufacture of adhesives are reported<sup>141</sup>.

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## Chapter 10

### Adhesives from Protein Substances

Adhesives from protein substances were among the earliest used commercially, and are still popular and widely used. The manufacture of casein glue appears to have its origin in Switzerland and Germany during the early part of the nineteenth century, and since that time a large amount of work has been accomplished in producing the necessary refinements to bring it to a satisfactory state of development. Major fields of application for the protein adhesives are in the manufacture of certain grades of plywood and as a general purpose material for wood bonding. Since the advent of synthetic resin adhesives, protein adhesives have suffered in comparison when questions of weather and moisture resistance prevailed, though there are still many applications for which the protein types are best. Probably the largest use of casein in this country is in manufacture of coated paper.

In this chapter, emphasis will be placed on relationships between protein adhesives and the synthetic resins, as well as those attempts to improve water resistance of protein-base materials. More comprehensive evaluations of protein adhesives appear elsewhere<sup>1, 2</sup>. Casein, soybean protein, and albumin-base substances will largely form the subject matter of this chapter.

#### Casein Adhesives

While furniture applications have been known for many years casein base adhesives were first employed to a limited extent for cementing wooden aircraft assemblies during the first World War because they were the strongest and most weather resistant at that time. First patent reference to casein glues in the United States appeared early in 1876<sup>3</sup>. Casein is precipitated from skim milk as a curd which is thoroughly washed and dried, and then ground to pass a number 20 mesh screen or finer for glue manufacture. The principal constituents are casein, water, hydrated lime, and sodium hydroxide, though numerous other modifying agents are employed to bring out certain desirable qualities.

Without the addition of sodium hydroxide, casein glues have a limited working life, though a high strength adhesive of good water resistance is

obtained. On the other hand, a practical working formula may combine certain proportions of sodium hydroxide and calcium hydroxide to obtain good water resistance and convenient working life. The latter forms an irreversible gel with the casein, and is desired as a constituent because it does not dissolve too fast and reaction is slow, forming calcium caseinate. More soluble calcium salts form the caseinate too rapidly, while other irreversible gels have also been produced by barium hydroxide and magnesium hydroxide.

General classifications of casein adhesives are based upon their commercial form, and they are called "prepared" or "wet-mixed" adhesives. Prepared glues are usually sold in the form of a powder in which all the dry constituents are mixed, requiring only the proper addition of water. Generally about 1 part of powder is slowly added to 2 parts of water at room temperature, accompanied by adequate mechanical stirring. The casein adhesive is then ready for use and will have a working life of usually less than one day. Proportions recommended by the manufacturer of the adhesive should not be altered by adding more water to thin out or extend life, if strong, reliable joints are to be made.

Wet-mix glues require a little more skill in their preparation, but by following the correct proportions as well as recommendations for the order of stirring the constituents in, good results are obtained. The casein is usually allowed to soak in water, followed by the alkaline agent, such as sodium hydroxide, in additional water to promote complete solubility. This may be followed by agents which will form irreversible gels, such as calcium caseinate, though solutions of casein in alkalies can be used as glues alone. In solutions of strong alkalinity, the casein hydrolyzes, much of it splitting into its primary cleavage products. Glued wood joints comparable in strength to animal glues are obtained, though neither possesses good water resistance. With high lime content there is a tendency toward staining. Typical water-resistant casein adhesives prepared by Buttermann and Cooperrider<sup>4, 5</sup>, represented an improvement over earlier types, though still much less satisfactory than the synthetics.

Browne and Brouse<sup>1</sup> analyzed a large number of casein adhesive formulations and broke them down into the following groupings:

#### Casein—Water, plus Direct Alkali

Casein	100 grams	Characteristics: High strength, poor water resistance
Water	300 grams	
Sodium hydroxide	8-10 grams	
(dissolve in part of H <sub>2</sub> O)		

The time for swelling the casein as it is soaked in water is about 10 minutes, though this depends upon the fineness with which it has been

ground. Consistency may be varied by the addition of more water, though lumping will occur if more casein is added directly. Water-soluble ammonium salts of strong acids increase the viscosity of the adhesive even more. By altering the ratio of alkali to casein the viscosity can be altered at will, higher viscosities being attained with lower alkali concentrations.

### Casein—Water plus Alkali Indirectly

In preparing a ready mixed adhesive formulation with casein so that only water will have to be added to make it ready for use, the alkali may be introduced in an indirect manner. One way to do this is to replace the sodium hydroxide with a chemically equivalent amount of calcium hydroxide and a substance which, dissolved in water, reacts with calcium hydroxide to form sodium hydroxide. A number of sodium salts have been proposed which do not react with calcium hydroxide or casein when dry, including sodium oxalate, sodium tartrate, sodium citrate, sodium salicylate, sodium phosphate, sodium sulfite, sodium stannate, sodium arsenite, and sodium fluoride. By increasing the proportion of calcium hydroxide, water resistance is improved materially, though working life may be cut down. The formulation may be expressed as follows:

Casein	100 grams	Characteristics: High strength, low water resistance, good dry storage (prepared mix).
Calcium hydroxide	7.4 grams (0.2 gram equivalent)	
Sodium salt	0.2 gram, equivalent	
Water	300 grams	

### Casein—Water, plus Salt Hydrolyzable to Alkali

The introduction of freely hydrolyzable salts into a casein adhesive formulation is still another method of adding the sodium hydroxide indirectly. Brouse and Browne cite a large number of patent references to borax, sodium phosphate, sodium hyposulfite, sodium tungstate, sodium aluminate, sodium salts of weak organic acids, sodium resinate, and sodium arsenate. The casein reacts with the sodium hydroxide liberated by hydrolysis of these salts to form sodium caseinate, permitting further hydrolysis of the salt.

### Casein—Water, plus Sodium Hydroxide, plus Calcium Hydroxide

The formation of calcium caseinate is generally preferred in commercial casein adhesives of improved water resistance. An irreversible gel is formed which possesses good water resistance, though which increases the problem of establishing a good working life. Dunham and Lindauer were among the first to recognize the specific advantages of calcium hy-

droxide in increasing the water resistance of casein adhesives<sup>6, 7</sup>. Following proportions are representative:

Casein	100 grams	Characteristics: Improved water resistance, good strength, limited working life.
Water	250 grams	
Sodium hydroxide	11 grams	
Calcium hydroxide	20 grams	

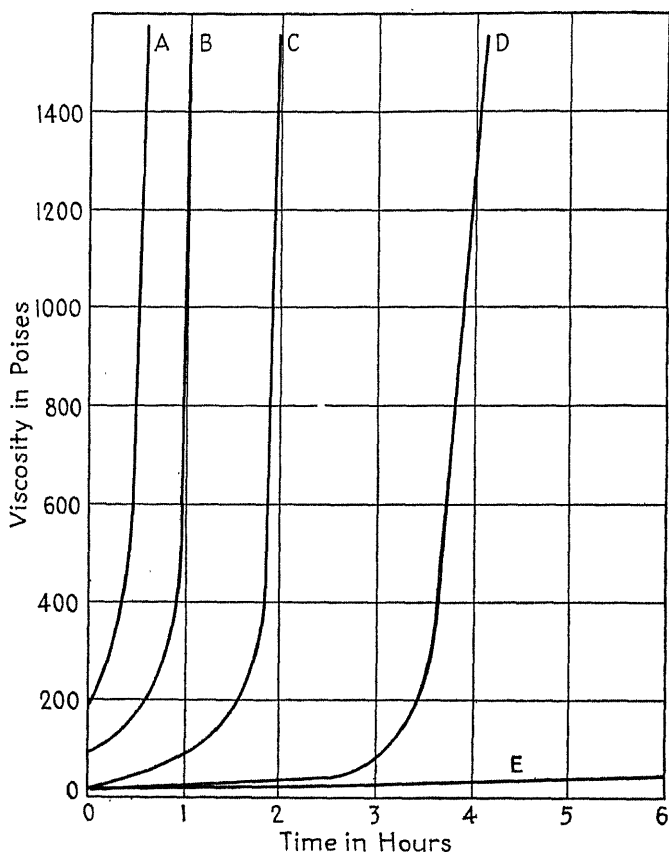


Figure 35. Change in viscosity after mixing of Casein glue: 100 gr. casein, 300 gr.  $H_2O$ , 15 gr. of  $Ca(OH)_2$ , plus NaOH as noted.

A = 4 gr. NaOH, B = 6 gr. NaOH, C = 8 gr. NaOH, D = 10 gr. NaOH, E = 12 gr. NaOH. (After Brown and Brouse)

Calcium hydroxide appears to have the proper balance in such formulations, and does not dissolve too rapidly to form irreversible gels. Working life is generally short, though this is controlled to a large extent by the proportion of sodium hydroxide. Varying the alkalinity from 4 to 12 grams of sodium hydroxide (0.1 to 0.3 gram equivalent) per 100 grams of

casein in a formula resembling the one above, Brouse and Browne show the change in viscosity of casein adhesive after mixing (Figure 35).

### Casein—Water—Calcium Hydroxide—Sodium Silicate

Casein adhesives formulated with sodium silicate differ quite markedly from other types in that less sodium hydroxide is required to attain a given working life. The amount of calcium hydroxide present is not as critical as in other examples, inasmuch as the presence of silica tends to retard the formation of the casein jelly. The sodium silicate commonly used has a silica-soda ratio of 3.25/1 and a density of approximately 40°Bé at 20°. This combination serves well as a wet-mix glue, though it is less satisfactory as a dry mix activated by water. The following combination developed by Buttermann<sup>4</sup> has good working properties and has served as the basis for many additional formulas:

Casein	100	Characteristics: Good working life, good strength, water resistant.
Water	200	
Calcium hydroxide	20-30	
Water	100	
Silicate of soda	70	

The addition of a small amount of copper salt has been found effective in obtaining uniformly good values of water resistance<sup>5</sup>. Buttermann and Cooperrider recommend adding 2 to 3 parts of cupric chloride in 30 to 50 parts of water to the above formula. The copper salt solution is the last ingredient to be incorporated; the others are added in the order listed in the formula above. Less calcium hydroxide is permitted when the copper salt is used without affecting water resistance. Cupric sulfate may be substituted for copper chloride. This adhesive has proven durable in warm, damp atmospheres, and unfavorable to growth of micro-organisms. It has been suggested that copper salt serves as a preservative under these conditions.

While ammonium hydroxide may be used to replace sodium hydroxide, considerably more water must be added to secure a glue of the same viscosity. Generally the working life is shortened, unless the proportion of calcium hydroxide is substantially reduced, which impairs the water resistance.

A neutral casein solution may be obtained by dissolving casein in an aqueous solution of urea. Formaldehyde has been added to improve water resistance<sup>8</sup> and rubber latex may be included to develop an adhesive for cellophane tape<sup>9</sup>. Various aldehydes have been added to casein glue from time to time in an effort to improve their water resistance, though results have not reached the same importance in wood working as formulas

discussed on the preceding pages. Harvey recommended formaldehyde and hexamethylenetetramine in casein adhesives<sup>10</sup>, while Bradshaw proposed a casein-calcium hydroxide-water formula with a minor amount of an aldehyde and soluble copper or nickel salts<sup>11</sup>.

Pierson developed an adhesive for woodworking purposes by combining with the casein ammonium sulfo-cyanate and 2 to 40 per cent paraformaldehyde based on the weight of the casein<sup>12</sup>. It is likely in this example that some reaction also took place between the paraformaldehyde and ammonium sulfocyanate. This adhesive was characterized by good fluidity over a long period. Christopher broadly claimed adhesive mixtures of casein, biuret, and water and subsequently specified the addition of an aldehyde to this combination<sup>13</sup>. Satow retarded the coagulating action of formaldehyde on casein by adding ammonia to form unstable amide compounds<sup>14</sup>. On the other hand, it has been reported<sup>15</sup> that gelatinization is prevented by the addition of small amounts of furfural.

Urea-formaldehyde condensation products dissolved in an alkaline medium are blended with a protein material such as casein to form useful adhesives<sup>16</sup>. The blending of urea- and phenol-formaldehyde with casein has been practised in the formation of moldable plastic products. Brother and McKinney listed numerous patent references bearing on this phase of the art, in discussing their contribution of adding a formaldehyde-hardened product to a synthetic resin<sup>17</sup>. Abramowitsch tried to circumvent the difficulty of adding formaldehyde to casein glues, by selecting an isoelectric casein (1000 grams), 0.2-1.0 gram-moles of formaldehyde and 0.3-1.0 gram-moles equivalent of sodium hydroxide or basic salts<sup>18</sup>. Brims prepared plywood adhesives of the following proportions<sup>19</sup>:

Casein	100 parts (wgt)	Casein	100 parts
Urea	15	Sodium phosphate	4
Water	460	Urea	15.5
Formaldehyde	7.5	Water	480
		Formaldehyde	8

Lee and Erikson developed an interesting technique for reacting formaldehyde with a protein such as casein or soybean. Using a volatile base such as ammonium hydroxide or ethylamine, they dissolved the casein and added an acetal, *e.g.* diethyl acetal. Lactic acid or glycolic acid was added to decompose the acetal to an aldehyde, when the film became acid upon evaporation of the volatile base. The aldehyde insolubilized the protein<sup>20</sup>. Julian also produced a protein-formaldehyde solution with delayed gelling properties<sup>21</sup>.

#### Miscellaneous Additives to Casein Adhesives

Various chemicals have been proposed for improving certain qualities of casein adhesives. Salicylic acid and calcium hydroxide are suggested

in one specification<sup>22</sup>, while Bradshaw recommends aromatic sulfonic acids to prolong the working life of the adhesive<sup>23</sup> with various zinc compounds for accelerating setting. The value of casein as a protective colloid in rubber latex adhesives has long been recognized as an advantage to the rubber, and effective combinations of both have been produced.<sup>24</sup>

In developing an adhesive for regenerated cellulose film, Charch and Snyder combined synthetic resins with water-miscible materials. Aqueous solutions of casein and gelatin were combined with glyceryl phthalates and a small proportion of non-drying oil to form an adhesive for cellophane<sup>25</sup>. The inclusion of substantial amounts of clay and other inert materials contributes to an improvement in the strength of casein adhesives, it has been claimed<sup>26</sup>. The colloidal clay comprised 10 to 30 per cent by weight of the casein present. Calcium hydroxide and sodium fluoride were present to dissolve the casein and improve its water resistance. Advantages are also claimed for the addition of butylated naphthalene sulfonic acid to the alkali-dissolved casein adhesive<sup>27</sup>.

Addition of water-soluble polyhydric alcohols such as glycerol renders the casein adhesive more flexible<sup>28</sup>; triethanolamine lactate was recommended for this purpose in place of glycerol<sup>29</sup>. Harris claimed that casein was altered chemically by heating with a polyethylene glycol<sup>30</sup>. By heating casein with twice its weight of glycerol and 1.0 per cent of sodium hydroxide to 150 to 165°, a clear liquid was obtained which was used as a safety glass adhesive<sup>31</sup>. Sodium metasilicate in combination with a small proportion of sodium hydroxide is employed effectively in dissolving casein in the manufacture of casein adhesive; the ratio of alkaline oxide to silicic acid is 1 to 1<sup>32</sup>. A neutral adhesive paste for tin surfaces is prepared from a casein solution and sodium borophosphate<sup>33</sup>. The addition of carbon disulfide to casein glues has been observed to improve water resistance<sup>34, 35</sup>. This is a rather important step for soybean protein adhesives and is discussed more fully later. Zein dissolved in water and alcohol is also stabilized by the addition of carbon disulfide<sup>36</sup>.

Dried milk has been introduced as adhesive material, sometimes in combination with casein<sup>37</sup>. Sodium hydroxide and calcium hydroxide are employed, as in the conventional art, though the dried milk causes long assembly times and working life. Good, stable adhesives have been prepared by digesting casein with a solution of sodium silicate<sup>38</sup>. Ordinarily, however, heating of casein solutions is not practised. Casein and other protein adhesives are stabilized by antioxidants extracted from finely divided unbleached cereals, nuts and seeds<sup>39</sup>.

When protein adhesives are employed in conjunction with metal surfaces, Brown recommends the addition of a chromate or dichromate salt if the metal is likely to corrode in the presence of an alkali. Aluminum-to-plywood assemblies may thus be prepared<sup>40</sup>. Halls discussed a number

of casein adhesives and their formulas<sup>41</sup>. Guth employed protein adhesives to bond abrasive grains, specifying the use of ethylene glycol or diethylene glycol, or glycerol as a flexibilizer<sup>42</sup>.

An adhesive capable of remaining flexible and pliable indefinitely was prepared from 90-mesh casein, a mild base (triethanolamine) and glycerol as a plasticizer. The glycerol was specified as 20 to 30 per cent of the total<sup>43</sup>. This adhesive resisted oils and greases. For use as a paper coating or cold water paint, calcium carbonate, casein, and starch were employed together<sup>44</sup>. As a label adhesive stable against putrefaction, casein plus an organic amide (urea or formamide), zinc oxide and sodium hydroxide were formulated to yield an adhesive with a good working life<sup>45</sup>. Liquid monohydric alcohol aliphatic alcohol esters of rosin are recommended as plasticizing agents for protein adhesives<sup>46</sup>. A stable bonding adhesive for metal parts is prepared from rubber latex and casein and used commercially ("Casco"-NT-442). Good flexibility at temperature extremes is apparent.

### Preservatives for Casein Glues

One objection which has always prevailed for casein adhesives has been lack of resistance to mold and fungi growth, attendant upon continuous exposures to high humidity. It was pointed out earlier that the presence of soluble copper salts in the casein adhesives improved resistance to bacteria growth, though compared to the resistance of synthetic resin adhesives, casein adhesives have suffered. As early as 1925, experiments were started at the Forest Products Laboratory to show the effect of adding preservatives to casein glue in order to increase its durability under exposure to high humidities. Ten per cent of beta naphthol or 20 per cent of creosote based on the weight of the dry glue powder showed promise as preservatives<sup>47</sup>.

In a series of investigations in Germany, Hermann considered thymol best suited as a preservative for casein adhesives<sup>48</sup>. In comparing the mold resistance of casein-glued plywood, sodium fluoride, thymol, lead nitrate, copper chloride and other substances were compared. Best results were obtained with 3 per cent of thymol, though casein was still inferior to the mold resistance of a phenol-formaldehyde resin adhesive<sup>49</sup>.

Even better mold resistance is obtained with some of the more recently developed preservatives such as chlorinated phenols and their sodium salts. Retention of more than 80 per cent of the original dry strength for nine months' continuous exposure at 80°F and 97 per cent relative humidity by casein glues is reported with 5 per cent of pentachlorophenol as a preservative<sup>50</sup>. The same commercial glues without the benefit of the preservative characteristically decreased markedly in strength under the same

conditions of exposure. However, the resistance to soaking in water is not improved by the preservative. Some of the data reported in the above reference<sup>50</sup> are reproduced in Figure 36. Curve A is casein glue +5 per cent pentachlorophenol—and none for curve B. However, under conditions involving high temperature and high humidity (158°F and 60 per cent relative humidity) and under repeated cycles of exposure at room temperature and 158°F, no differences in dry original strength of the casein adhesive with or without preservative were reported<sup>50</sup>.

In describing the technique of measuring the mold resistance of protein glues, Kaufert recommends immersing plywood shear test specimens for  $\frac{1}{2}$  to 1 minute in a water suspension of mold spores prepared from moldy veneers previously inoculated. A period of incubation at 72 to 80°F

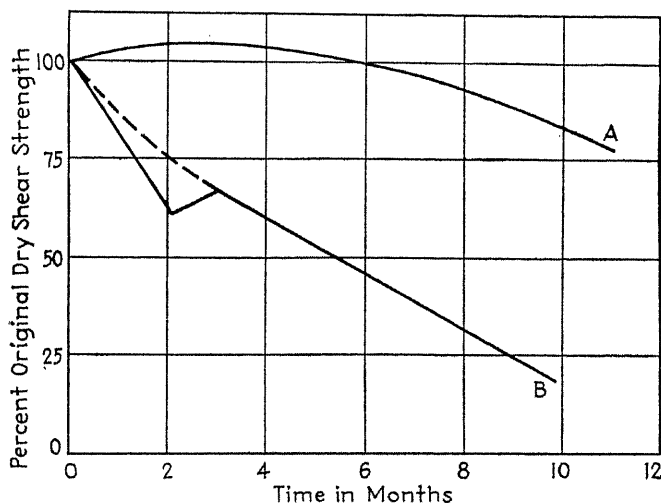


Figure 36. Effect of 80°F–97 per cent relative humidity on casein glue. (Curve A) 5 per cent pentachlorophenol. (Curve B) no preservative. (Data by *Wanguard*)

follows. Some of the data reported in Kaufert and Richard's paper are tabulated herewith<sup>51</sup>:

Results of Mold Exposure Tests on Casein Glued Yellow Birch Sapwood Plywood Shear Specimen<sup>51</sup>.

Preservative Added to Casein Glue	Original Dry Shear (psi)	After Exposure for	
		14 days (psi)	28 days (psi)
None	501	48	0
5.0% sodium tetrachlorophenolate	508	310	354
5.0% sodium trichlorophenolate	514	363	274
5.0% sodium orthophenylphenolate	504	276	80
5.0% orthophenylphenol	430	359	216

Improvements were also noted in soybean protein adhesives on the addition of a preservative. Within recent years there has been much interest in the improvement of casein adhesives, particularly where their applications were on products being sent to tropical regions. Of course, the urea-formaldehyde and phenol-formaldehyde have been outstanding in their resistance to weather exposure and in their mold and fungi resistance; long experience with casein adhesives in wooden assemblies has prompted fabricators to try methods of employing and improving upon the protein materials.

There have been comparisons drawn between casein glues and cold-setting urea resin glues for joints in aircraft assemblies<sup>52</sup>. After examining more than 1800 specimens it was concluded that the cold set urea-formaldehyde resins were capable of producing bonds whose dry strength and high percentage of wood failure compared favorably with casein glues. The urea resins, however, have the additional advantage of greater water and mold resistance.

In a more recent comparison of cold-setting synthetic-resin adhesives compared to casein, the latter fell off most markedly in strength, though were better than the urea-formaldehyde types in regain of original dry strength upon drying. Phenol-formaldehyde resin adhesives were considerably superior to both these types in wet strength and the retention of strength after drying, even after a number of repeated cycles<sup>53</sup>.

### **Soybean Protein Adhesives**

Soybean protein adhesives have enjoyed a large scale specialty application in this country as bonding agents for interior type Douglas fir plywood. They have not been employed as extensively or in as many diverse applications as casein protein adhesives, though the developments leading to their commercial utilization throw much light on the art of adhesive manufacture. Brother, Smith, and Circle have published a comprehensive resume and bibliography on soybean proteins, with a section devoted to adhesive developments<sup>54</sup>. It has been pointed out that the consumption of soy-bean adhesives averages 34,000,000 pounds annually, making it one of the top-ranking adhesives in total volume produced<sup>55</sup>.

Adhesive materials from soybeans have been known for some time. Omura and Okada boiled and crushed soybeans and dissolved out the protein. This was used as a raw material for adhesives<sup>56</sup>. Following the technology of casein, Johnson soaked the soybeans in water, ground and boiled them, removed oil, and mixed them with lime, sodium fluoride and water<sup>57</sup>. Using ground soybean meal dissolved in aqueous alkaline solutions, Johnson separated the liquid portion, and after removing the oil, curdled the juice with an acid to liberate the portion effective as an adhe-

sive<sup>58</sup>. The precipitated portion was washed and dried, ground, and employed in adhesive manufacture. Laucks and Davidson contributed to the art of making waterproof soybean adhesives by reacting upon soybean flour (through 100 mesh) sodium hydroxide and calcium hydroxide, the latter contributing to the formation of an irreversible gel. Carbon bisulfide or polysulfide is also claimed to be helpful in waterproofing<sup>59</sup>. A typical composition found satisfactory for bonding wood veneers follows:

Soybean flour	30 (wgt.)
Water	120
Sodium hydroxide	13 (18% solution)
Carbon bisulfide	5
Calcium hydroxide	3
Sodium silicate	15
Copper sulfate	1
Water	5

Dike patented a large number of features of the technique of applying soybean flour to bonding plywood<sup>60</sup>. He described the treatment of the surface with discrete particles of soybean flour, transformed by heat and pressure above 212°F. Various additives are proposed, including blood albumin, and various alkalies are suggested for the final formula.

Several tanning agents have been reacted with soybean proteins to improve their water-resisting qualities, including aluminum and chromium salts<sup>61</sup>, tannins<sup>62</sup>, quebracho<sup>63</sup>, and tannic acid agent<sup>64</sup>. Adding slaked lime to the caustic dispersion of the soybean protein adhesive as well as salts hydrolyzable to the alkali promises improvements in this respect. Sodium sulfite<sup>65</sup>, sodium dichromate<sup>66</sup>, and rosin<sup>67</sup> also improve water resistance. Treatment of soybean protein in the colloidal state with sodium hydroxide and zinc chloride has been practised to improve the qualities of the adhesive products<sup>68</sup>. The soybean cake from the oil extraction forms a coarse meal, which is dried and then treated with live steam prior to processing into adhesives<sup>69</sup>.

Reaction of soybean proteins with aldehydes to improve their water resistance has been the subject of much investigation. Osgood investigated this subject<sup>70</sup>, and Isaacs employed small quantities of formaldehyde<sup>71</sup>. Cone and Galber developed a cold-press glue soybean flour and blood albumen dissolved in sodium hydroxide, to which formaldehyde had been added<sup>72</sup>. The foaming of the blood was repressed with terpineol. Aldehydes and carbon bisulfide were employed as gelling agents for soybean adhesives<sup>73</sup>. Small percentages of ammonia or sodium sulfite retard the action of formaldehyde<sup>74</sup>. In preparing the latter adhesive, Satow grinds the components to pass through 100 mesh (soybean flour 100, sodium phosphate 10, sodium fluoride 5, calcium hydroxide 7 to 10, cal-

cium carbonate 50 and copper sulfate 0.5), and adds three times its weight of water when ready for use. To this is added 5 to 10 parts of the reaction product of formaldehyde and ammonia, for example; a glue the consistency of which remains unchanged for 6 hours is obtained. It is claimed that within 24 hours after the addition of the adhesive to wood a shear strength of 380 to 480 psi is obtained in the dry state and 200 to 250 psi in the wet state.

In examining the use of soybean protein in the paper industry, Smith and Max point out that this protein material is more tolerant of formaldehyde than the casein and less readily gelled<sup>75</sup>. The aldehyde may be introduced indirectly, *e.g.*, with the addition of diethyl acetal to form aldehyde under acidic conditions<sup>76</sup>. Smith, Max, and Handler found it possible to disperse the soybean protein in aqueous formaldehyde solution—a technique which should contribute to the formation of improved adhesive products<sup>77</sup>. Brothier and McKinney showed that soybean protein hardened with formaldehyde near its isoelectric point (pH 4.1) produced a material with minimum water absorption and thermoplastic qualities<sup>78</sup>. This is also the point of maximum protein recovery from various dispersions<sup>79</sup>. The protein liberated at pH 4.1 has been specifically employed as an adhesive material, low solution viscosity and high adhesive strength being claimed<sup>80</sup>. Hieronymus treated the soybean meal with sodium hydroxide for several hours, added hydrogen peroxide which reduced the viscosity of the colloidal suspension, and then precipitated the protein for subsequent use as an adhesive<sup>81</sup>. In Figure 37 the precipitation of soybean protein from water and alkali dispersions by treatment with sulfuric acid is indicated. Data are taken from references 79 and 54.

Laucks and Davidson discuss the art of soybean protein adhesives in one of their later patent specifications<sup>82</sup>. They felt that casein adhesives were too costly for plywood manufacture and not as uniform as others due to the variety of sources. In their development of a waterproof adhesive, they implied the production of plywood which would not withstand indefinite exposure to water, but which could be soaked for 72 to 100 hours in cold water without coming apart<sup>59</sup>. They stated that the chemicals employed in making casein glue, *viz.*, lime and sodium silicate, do not give as good results with soybean flour as casein, and indicate a preference for caustic soda and lime, and the addition of carbon bisulfide for waterproofness. The latter agent tends to thicken the glue, though by suitably controlling the proportion of caustic soda content the thickening tendencies may be controlled. The caustic soda is kept within the limits of 3 to 17 per cent of the soybean flour weight, and the carbon bisulfide from 1 to 6 per cent<sup>82</sup>.

In a recent development of cold-press plywood, a soybean adhesive

(Laxein soybean No. 90) is applied under the following schedule: Cold press 15 minutes at 175 psi, roll out of press and store for 6 hours before sanding or sawing<sup>83</sup>. This new process eliminates the handling of approximately 40,000 pounds of clamps per eight-hour day. Cold-pressing of casein adhesives or earlier soybean types, for example, required considerable floor space in the plywood plant and storage facilities. The speed-up of closed assembly time is a noteworthy advance in the art.

Soybean adhesives have been employed in conjunction with a starch base<sup>84</sup> and casein dispersions<sup>85</sup>. Phenol-formaldehyde resins in conjunction with soybean<sup>86</sup> as well as urea-formaldehyde resins<sup>87</sup> have been de-

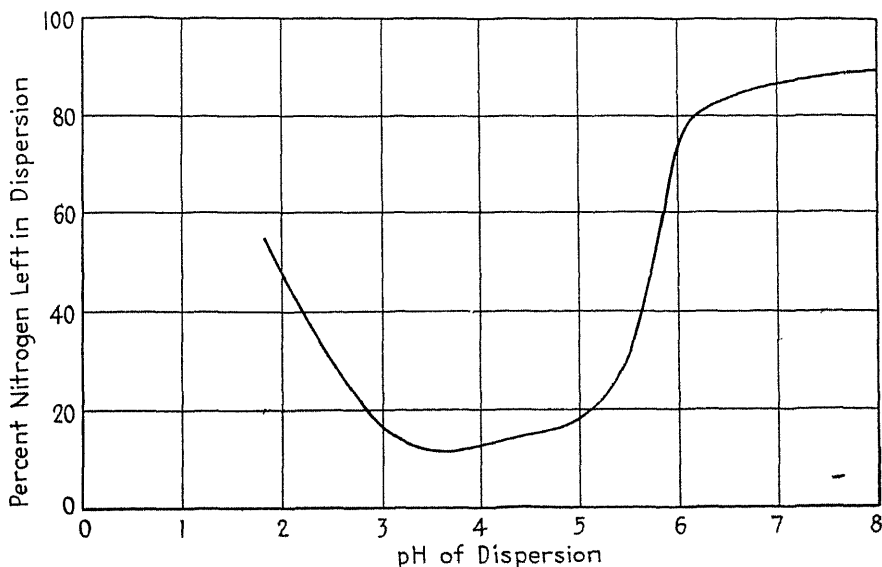


Figure 37. Precipitation of soyabean protein from water by sulfuric acid. (After Smith and Circle)

scribed. Considerable attention has been given to the combination of soybean adhesives with blood albumin. Dike and Dunham<sup>89</sup> described an adhesive of this type, employing powdered blood albumin and powdered soybean flour<sup>88</sup>. Cooper found in using protein adhesives that insoluble particles of dried blood sealed wood veneer surfaces and prevented "starved joints"<sup>90</sup>. Hadert reviewed a number of significant casein adhesive formulas, including casein-blood albumin blends<sup>91</sup>. Using cotton seed flour, a water solution of blood albumin, sodium metasilicate, and hydrated lime, a useful plywood glue has been developed by Cone<sup>92</sup>. The contributions of blood albumin to the field of adhesives are discussed at the end of this chapter.

### Miscellaneous Proteinaceous Materials for Adhesives

A number of non-fibrous protein materials have been employed in the manufacture of adhesives, though only two, casein and soybean, have attained any large volume. Among the lesser known protein-base adhesives are those derived from the peanut protein, zein, and from corn gluten. Bradshaw uses sodium carbonate and sodium fluoride to dissolve proteaginous peanut meal in preparing an adhesive<sup>93</sup>. In manufacturing the peanut protein for plywood adhesive, sodium hydroxide in quantity 3 to 8 per cent of the peanut meal and water 3.5 to 3.8 of the dry glue base were specified<sup>94</sup>. A protein adhesive plus powdered ivory nut served as the basis for an alkali-soluble glue<sup>95</sup>. Wheat flour, portland cement, and soybean protein served in another example<sup>96</sup>.

The flour of coffee bean hulls came in for its share of attention, possessing a price advantage over other types such as soybean and casein, it was claimed<sup>97</sup>. The ground flour, an alkaline solvent, water, and carbon bisulfide made an excellent adhesive. In order to expedite the setting qualities, china clay and zinc oxide were added. Crude corn gluten, obtained as a by-product of cornstarch manufacture, has also been employed to a limited extent in adhesives, sometimes in conjunction with starch<sup>98</sup>. Sturken developed a wood adhesive from zein, formaldehyde, and an organic acid. This required heat and pressure to cure<sup>99</sup>. Zein in a concentration of 20 to 35 per cent was dissolved in an aqueous organic solvent, while 2 to 50 per cent of formaldehyde and 2 to 100 per cent of acetic acid were specified. One use described was the uniting of glass sheets in an application of zein adhesive. A water-resistant zein preparation was obtained by dissolving zein in alcohol and mixing with wax and hydrocarbon solvent for the latter. This was used for adhesive purposes<sup>100</sup>. An adhesive for wood veneers and paper contains 20 to 35 per cent of zein in 2 to 50 per cent of alcohol containing 20 per cent of formaldehyde based on the zein<sup>101</sup>.

Swallen discussed other adhesive applications of zein, which had been extracted from corn gluten by isopropyl alcohol<sup>102</sup>. Zein has free carboxyl, amino, and amide groups, and may be cured with formaldehyde or formamide. Up to 50 per cent of ester gum improves the flow in laminating. Close claimed advantages for zein over peanut meal and soybean in the manufacture of adhesives for wall paper. He developed an emulsified form of the adhesive with the aid of wood rosin and ammonium hydroxide<sup>103</sup>. The proportions by weight were as follows:

Water	30-70
Zein	3-8
Wood rosin	2-7
Ammonium hydroxide	1-8
Hydrogen peroxide	0.1-1.0

The condensation products of fatty acids with monoethanolamine, when added to protein base adhesives, are claimed to increase water resistance, strength, and spreadability; they change the texture of the glue line from a grainy mixture to a smooth-flowing consistency<sup>104</sup>. White employed a small amount of copper sulfate and a sulfonated oil (2 per cent of dry glue) to increase the wet strength of adhesives from cottonseed meal and soybean flour<sup>105</sup>. Hemp seed proteins and rape seed proteins in adhesive manufacture for plywood have been described in a bulletin of the Forest Research Institute in India<sup>106</sup>. Formaldehyde was also employed to modify these adhesives.

Evans and Manley did a considerable amount of work in stabilizing zein dispersions against gelation<sup>107</sup>. They examined a large number of single and mixed solvents, which after the dispersion of zein tended to set spontaneously with time to a solid gel. Stability is improved by anhydrous solvents and low temperature storage, and by a 15 minute heating immediately after dispersion. Swett prepared a zein cement from equal parts of zein and rosin<sup>108</sup>. Zein has also been stabilized from gelling by a water soluble thiocyanate<sup>108a</sup>. Evans has modified zein by reacting zein with formaldehyde, air drying, followed by baking<sup>108a</sup>.

Water-resisting glues from fish meal (after removal of oil) and specifically from the protein bearing parts of the body, have been prepared<sup>109</sup>. From 50 to 70 per cent of protein material are present in the meal. The fish meal, plus hot water, sodium hydroxide, zinc chloride, lime (reacts with saponified oils) and cold water to desired consistency, form the adhesive composition. Campbell prepared adhesives from fish offal after reaction with acetic acid<sup>110</sup>. Brothier and Binkley have developed a process for preparing adhesive products from keratin<sup>110a</sup>.

### Blood Albumins in Adhesives

Blood albumin by itself or in combination with other adhesives has figured prominently in the development of plywood adhesives, particularly those of the hot-set variety. Some of the examples of combinations of blood albumin with protein adhesives have already been cited in this chapter. Real activity in blood albumin glues dates from 1917 when there was a marked demand for a water-resistant plywood. They are mixed at time of using and consist of fresh blood of slaughtered animals or dried, soluble blood albumin. Reviewing miscellaneous developments we observe the following:

Blood albumin, hexamethylenetetramine and animal glue or gelatin formed the basis for a plywood adhesive<sup>111</sup>. Forty-five parts of black albumin (dried blood) are combined with 55 parts of water, and then 9 per cent of sodium silicate based on the albumin are compounded to form an adhesive for joining wood veneers<sup>112</sup>. Stadlinger reviewed protein ad-

hesives, finding highest strength from those derived from leather scrap. He dissolved albumin in cold or warm water and applied it to wood veneers. The albumin coagulated around 68 to 70°. Calcium hydroxide, ammonium hydroxide, and ammonium chloride were reported to improve its adhesive properties<sup>113</sup>. The blood albumin has even been prepared in thin film form for the purpose of united wood veneers<sup>114</sup>. Biddle combined proteins and albumin in conjunction with rubber latex to form adhesive products<sup>115</sup>.

Formaldehyde and ammonia added to albumin in conjunction with cobalt and chromium oxides were claimed to improve the water resistance of albumin adhesives<sup>116</sup>. The adhesive is brushed or sprayed on. The presence of cobalt oxide, it is claimed, not only improves the adhesion to the laminae, but also makes the material quite hard. Soybean flour, blood albumin, alkali, and formaldehyde appear together as another adhesive product<sup>117</sup>. Wood adhesives have been formed by combining blood or blood albumin with a urea-formaldehyde condensation product. Ammonium chloride was employed as a hardening agent<sup>118</sup>. The application of blood albumin to sodium silicates has attracted some attention<sup>119</sup>, as well as their use in phenolic resins<sup>120</sup>. Acidic hardening agents, urea-formaldehyde resins, and up to approximately equal weight of blood albumin were some of the features in a special adhesive by Menger<sup>121</sup>.

In more recent developments, fertilizer blood and water-soluble blood albumin are combined in the presence of an alkali to form an adhesive<sup>122</sup>. At least 25 per cent of glycerol added to a blood albumin-formaldehyde mixture forms a good plywood adhesive, permitting better flow during the application of heat<sup>123</sup>. Addition of corn syrup to blood albumin adhesives also gave good results<sup>124</sup>. The color and odor are two practical objections to blood albumin adhesives.

In the preparation of blood albumin glues, it is important to let the dried albumin soak an hour or more before the addition of the other constituents, and if the insoluble proportion is too large, it may have to be filtered out. Insoluble matter increases with age. While blood albumin and water alone make a good glue, improvements may be achieved by other additions as already noted. Henning for example, prepared blood albumin for hot press work by the following formula<sup>125</sup>:

100 parts black soluble blood albumin (90% solubility)  
180 parts water  
4 parts ammonium hydroxide (sp. gr. 0.90)  
3 parts calcium hydroxide

Stir the above slowly to avoid excessive foaming. The slaked lime should not be excessive; otherwise, the solution may gel too rapidly. Consistency may be adjusted by varying the amount of water and blood albu-

min. To set this adhesive, a minimum temperature of 70° is required on the hot press. With a temperature of 100° and pressures of 100 to 200 psi good gluing of plywood has been obtained<sup>126</sup>. Hot-pressing of casein and blood albumin were extensively practiced abroad prior to 1930, though very little was done in this country up to that time.

Lindauer prepared a blood albumin glue with improved properties<sup>127</sup> comprising the following:

100 parts soluble blood albumin
140-200 parts water
5.5 parts ammonium hydroxide (0.90 sp. gr.)
15.0 parts paraformaldehyde

This adhesive has a working life of 5 to 6 hours before setting to an insoluble gel. Hot-pressing is recommended for this material. It was evaluated under different conditions of exposure in conjunction with a casein adhesive of low and high alkalinity<sup>128</sup>. Cycles of continuous soaking, exposure to high humidity, and cycles of low and high humidity were employed. The presence of paraformaldehyde apparently reduced the rate at which the adhesive hydrolyzed, and this adhesive exhibited much superior results to the two casein types examined. Reproducing some of the results of Brouse<sup>128</sup> in the following table, the superiority of the albumin-paraformaldehyde type is evident. The casein glue of low alkalinity was developed by Buttermann<sup>4</sup> (Forest Products Laboratory formula 11), while the other casein glue was a sodium fluoride-casein-lime formula:

Shear Strength of Yellow Birch Plywood. (Brouse)

Exposure Time	Exposed Continuously to 97% relative humidity		
	Casein Glue-Low Alkalinity (psi)	Casein Glue-Higher Alkalinity (psi)	Blood Albumin-Paraformaldehyde (psi)
Dry control	342	343	409
Wet control	255	196	361
1 month	279	132	379
2 months	65	22	330
4 months	72	40	328
8 months	0	0	313
12 months	0	0	270
24 months	0	0	216
36 months	0	0	135
	Exposed to Repeating Cycle (2 days soaking, 12 days at 30% R. H.)		
	Casein Glue-Low Alkalinity (psi)	Casein Glue-Higher Alkalinity (psi)	Blood Albumin-Paraformaldehyde (psi)
1 month	309	311	337
3 months	208	252	262
6 months	57	217	265
12 months	0	26	209
24 months	0	0	36

The decrease in strength was less pronounced in all cases for continuous exposure in water, though the advantages of the blood albumin-para-formaldehyde are noteworthy.

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## Chapter 11

# Vegetable Glues and Natural Resin Adhesives

Adhesives from vegetable and animal sources were known before the synthetic resin adhesives described in earlier chapters. Their early origin and their wide acceptance for miscellaneous adhesive problems have developed large markets and a large output of these materials. The amount of space which will be devoted to the subject of adhesives of vegetable origin may appear small in proportion to the earlier materials covered, when considering their present importance. This is not a reflection on the relative importance of vegetable adhesives, but rather evidence of the stated purpose of placing emphasis upon the more recent synthetic resin types.

Adhesives from vegetable sources constitute a rather large classification and will not include those of cellulosic origin which have already been covered. However, we shall dwell to some extent upon those of amylaceous origin, and upon those miscellaneous gums and exudations of vegetable origin which appear in modern adhesives. The relative position of starches and dextrans with respect to the adhesive field has changed in recent years, these materials giving way to newer types which possess better water resistance. However, there are a large number of applications to hydrophilic surfaces where the adhesives of vegetable origin are and will undoubtedly continue to be outstanding because of serviceability and low cost.

Another factor which will be examined is the application of water-dispersible vegetable adhesives as extenders and modifiers for synthetic resins and cellulosic derivatives, particularly those which are water-soluble at some stage of their application. This would include the urea and melamine formaldehyde resins, rubber latices, methylcellulose, and derivatives of polyvinyl alcohol. In this connection, examples of starch or dextrin additions to these materials as adhesives have already been cited in their respective chapters. New interest in the water emulsions of other synthetic resins, offer further possibilities of combining starches and dextrans for some specialty purposes.

In a recent review of starch adhesives, Smith and Hamilton made a thorough presentation of the highlights of the art, pointing out early use

of starch adhesives by the Egyptians and citing early patent references indicating the origin of the manufacture of starch in this country<sup>1</sup>. Bloede appears to be the first to produce dextrin on a commercial scale in the United States, manufacturing a mucilaginous compound by treating starch with nitric and hydrochloric acid<sup>2</sup>. The introduction of postage stamps in 1840 and the further appearance of gummed envelopes of the remoistenable type encouraged the development of adhesives of vegetable origin, which were ideally adapted to such applications because of the absence of health or industrial hazards. The science of vegetable adhesives has made remarkable strides during the last 20 to 25 years, replacing in many instances the animal glues which were the only ones used industrially until about 30 years ago. The vegetable adhesives appear especially suited to labelling and sealing by high speed automatic machinery for manufacturing corrugated boxboard, plywood, gummed tape, and for sizing paper and textiles.

### Types of Vegetable Adhesives

Starch forms the basis of most vegetable adhesives, varying from simple pastes made by boiling starch with water to those which have been treated chemically to form further derivatives. Included in the latter would appear various starch esters, such as the starch acetates. Perhaps the most simple and cheapest form of vegetable adhesive would be the flour paste, prepared from a finely divided flour (which includes protein and fat content). Various billposter's and paperhanger's pastes are prepared from these. Commercially, starch is derived from many plants such as cassava (tapioca), corn, sago, potato, wheat, sweet potato, etc. The chemical and physical properties of these starches vary, depending on their source and their method of manufacture. After washing and grinding, the starch granules are separated from the fibers and purified by settling in water.

Chemically, starch has the same constitution as cellulose, namely  $(C_6H_{10}O_5)_x$ . One of the best known concepts of the structure of starch suggests that the starch grain is built of small radially arranged crystallites; the chains continue to grow by the addition of new glucose units. A film is supposed to be formed around the whole by means of side branches between the chains, accompanied by esterification through the presence of phosphoric acid<sup>3</sup>. Following this thought, it may be pointed out that in a typical starch granule, the water-soluble core, the amylose, is surrounded by highly branched molecules and relatively insoluble film, called amylopectin. The processes of manufacturing starch adhesives are directed toward bursting of this film through various expedients. These processes may involve degradation of the starch molecule to dextrin, or if carried too far, to glucose.

The size and shape of the starch granules vary, depending upon their origin, as well as the ratio of amylopectin to amylose in a given material. Braude lists the maximum diameters in millimeters of the more common starches, ranging from .070 mm for sago starch to .014 mm for potato starch<sup>4</sup>. As water diffuses through the film, swelling the amylose, the film bursts and the amylose distributes itself as a colloidal dispersion, forming a paste. The temperature at which complete gelatinization occurs for a number of more common starches is shown in the following table. This of course is also dependent upon the relative purity of the material<sup>5</sup>, as gelatinization may take place over quite a range of temperature.

Starch	Temperature of Complete Gelatinization
Rice	72°
Corn	67
Wheat	62
Potato	72
Tapioca	64
Rye	56

Richter performed the above tests using 20 per cent concentrations of various starches. Nivling also did a considerable amount of work in evaluating these gelatinization temperatures<sup>6</sup>. The greatest amount of starch manufactured in the United States is from corn, which averages about 55 per cent starch. Considerable potato starch is also made, as well as some wheat starch. Cassava and sago starches are imported to some extent, the latter being used particularly for envelope gums<sup>7</sup>. Cassava starch is noted for the consistency of its paste and is most often used in the production of vegetable glues. Cassava belongs to a class of woody shrubs related botanically to the *Ceara* rubber tree. The shrub is processed in about two years after it has attained a height of 6 to 10 feet. The roots are tuberous and from these the starch is obtained. It has reached its greatest production in Java, though there was an unsuccessful attempt to cultivate the cassava plant in Florida<sup>8</sup>.

**Classifications of Starch and Dextrin Adhesives.** Starch and dextrin adhesives are generally classified according to the processing they received prior to compounding them into adhesives. The conversion from one form to another may be incomplete, leading to some overlapping manifested by variations in solubility characteristics:

1. Raw starch.
2. Starch dispersion with alkalis (may be cold or hot treatment and neutralized; may also include salts hydrolyzable to caustic soda).
3. Starch dispersion with acids (dilute mineral acids, followed by neutralization or treatment with alkali<sup>10</sup>).
4. Starch dispersion with salts (30° Bé  $\text{MgCl}_2$  or 40° Bé  $\text{CaCl}_2$ )<sup>9</sup>.

5. Starch dispersion with oxidizing agents<sup>11</sup>.
6. Enzyme (diastase) converted starch (best at 60–65°).
7. Dextrins.
  - (a) "British Gum", roasting of corn starch at 200°.
  - (b) Acidulation with dilute mineral acid; dry and roast at temperature depending on starch (140–175° for cassava, 125–140° for corn).

Most commercial dextrins contain some incompletely converted starch. Greater solubility and darker colors indicate higher degrees of conversion, though the iodine test for blue color is the most positive indication of the presence of starch. The presence of glucose must be at a minimum for best adhesiveness and reduced hygroscopicity. Because of greater solubility, the dextrin adhesives may replace starch adhesives where more rapid setting is required. Among the advantages of cassava starches, Dulac lists: lower cost, less odor, more stable, more viscous pastes, and better gelatinizing power<sup>11</sup>. Greatest bonding strengths are realized in starch dispersions which have not been converted to dextrins, and which possess high solids concentration. The functions of the processing treatments may be to make the starch grain more soluble by modifying its outer wall, or reduce its water-absorbing quality.

There is an innumerable variety of starch adhesives depending upon their origin and processing conditions, and the various methods which have been evolved for their manufacture have been directed toward the attainment of certain specific properties advantageous to certain applications. There are generally four main components to these adhesives: (1) the active component including the materials which produce gelatinization (see seven types just listed); (2) the solvent, generally water; (3) modifying agents such as water-soluble synthetic resins, borax, formaldehyde, proteins, wetting agents, etc.; and (4) plasticizers, which impart flexibility to the dry film.

**Preparation of the Starch Adhesive.** Vegetable adhesives are prepared in wet or dry form, though industrial preference is for the dry type. Whether the starting raw material is raw starch or processed starch, the adhesive preparation may follow one of three methods after the starch has been mixed with water:

1. Caustic soda and heat
2. Caustic soda at room temperature
3. Heat alone

Brouse describes one process in detail in the manufacture of a starch adhesive<sup>7</sup>. With heat approximately 3 per cent of sodium hydroxide may be used, though from 6 to 10 per cent of sodium hydroxide is used for a

cold conversion. In the former process after the required amount of water has been added and lumps of starch broken up, temperature is brought slowly up to 65° with adequate mechanical stirring. The starch changes in appearance from a white suspension to an amber-colored, stringy paste, which appears almost transparent on the end of a stirring rod. When it has reached this stage the reaction is stopped and the mass cooled to room temperature. The vegetable glue is quite viscous and requires the use of a mechanical spreader. The mixtures dry slowly and in some productions may be left in the glue spreader from day to day, capable of tolerating new additions from time to time. Slow setting means a long open assembly time, which is desirable, though this also means a long time under the clamps before it is safe to remove the parts being bonded.

The amount of water which may be used with the starch will depend upon whether it is a processed starch or a raw starch, the latter requiring larger proportions of water. A few typical proportions and formulas are listed below:

*Basic Soda-Starch Formula.*

Water	150 (weight)
Starch	100
Sodium hydroxide (36° Bé)	25
Water	25

Agitate one hour at 15 to 20° until a glassy mass is obtained. Keep temperature low if a thick mucilage is required. If temperature gets too high, due to the large concentration of caustic soda, the starch may break down into dextrin and have lower adhesive strength. To convert to a slightly alkaline ropy paste, suitable as a cheap starch adhesive, the following constituents may be added to the above formula<sup>11, 12</sup>:

Water	550
Borax	0.14
Hydrochloric acid (22° Bé)	5.0
Water	50.0

This gives a very high water-to-starch ratio of about 7.5/1; for some of the stronger adhesives prepared from processed starch this ratio is about 1.2 to 2.5/1. The Perkins processes in effect developed techniques of reducing the amount of water required, though they appear to have left the starch molecule intact. The acid pretreatment of starch by Perkins, followed by alkali treatment, is of special interest, inasmuch as the validity of the claims have been strongly contested<sup>13</sup>. It is acknowledged, however, that he was the first to produce a strong vegetable glue comparable to the animal glues and suitable for application on wood veneer.

In making adhesives from cassava starch, Perkins treats the starch

with an equal weight of water, heating the combination to 55° and adding 2 to 3 per cent of sulfuric acid with agitation. Care is taken to avoid dissolving the starch, and in 4 to 6 hours time, the mixture is neutralized and the starch dried. Treated in this manner, the water-absorptive power of the starch is substantially decreased<sup>13</sup>. This acid-treated cassava starch may now be suspended in water in the usual manner, and a glue formed by further treatment with caustic soda. For example:

Acid-treated cassava starch	200
Water	225
Sodium hydroxide	20
Water	30

The sodium hydroxide dissolved in some additional water is slowly stirred in at room temperature until a viscous semifluid consistency is obtained, adapted to use in glue-spreading machinery. Perkins specifically claims 3 parts or less of water in making his glue. Reiman disclosed vegetable glues as strong as animal glues<sup>15</sup>.

Considerable attention has been given from time to time to the employment of oxidizing agents in the manufacture of starch adhesives. Perkins disclosed the use of sodium peroxide<sup>10</sup>. Cassava starch is suspended in an equal weight of water and from : to  $\frac{1}{4}$  per cent of sodium peroxide is added, accompanied by an equal amount of sodium hydroxide. The mass is stirred for a long period of time at low temperature, filtered, dried at low temperature and applied in the development of adhesives as for the acid-treated starch. Bloxam employed potato starch and alkali per salts or peroxides, such as persulfate, percarbonate, perborate, and barium, calcium, and magnesium peroxide in processing his materials for adhesive manufacture<sup>14</sup>.

Harvey specifically recommended powdered barium peroxide in the manufacture of his starch adhesives<sup>16</sup>. In a typical starch adhesives designed for wood veneers, the following example employing barium peroxide is representative:

Cassava starch	84	Mix ingredients dry and add to 120.0 parts of water. Heat to 70° and when uniform add 2.5 parts of NaOH dissolved in 7.5 parts of water
Barium peroxide	0.5	
Soda ash	0.1	
Whiting	5.0	
Urea	10.0	

Dulac has done considerable work in incorporating hydrogen peroxide in the presence of sodium hydroxide into starch adhesive formulations. Liquefying of the starch occurs by oxidizing treatment and mechanical mixing<sup>17</sup>, though he recommends application of heat in some cases. Sodium fluoride is added as a preservative for vegetable glues, being stable,

odorless, and non-volatile. Formaldehyde is also added to improve storage characteristics. A strong glue prepared at room temperature by Dulac comprised the following proportions<sup>11</sup>:

Water	420	After mixing at room temperature add:	
Sodium bicarbonate	0.55	NaOH 36° Bé	70
Cassava flour	280	Water	70
Hydrogen peroxide	9	Turkey red oil	
		(ammonium salt, 90%)	0.65

Mix and stir the above for 12 hours.

Fuller prepared an adhesive product which resembled raw starch by using chlorine oxidizing agents in aqueous medium (sodium hypochlorite) and a nitrogenous inhibitor. Short, stable, starch solutions were prepared<sup>18</sup>.

White prepared a novel form of processed starch by passing an electric current through starch suspended in water. An acid was added to render the bath conducting, though the reaction was stopped before soluble starch was formed<sup>19</sup>. Stern developed a potential wood adhesive by reacting carbon bisulfide with starch partially converted with alkali<sup>20</sup>. Fackler and Gardner treated cassava flour suspended in water with phthalic acid, and heated it sufficiently to rupture the envelope surrounding the amylose, producing an adhesive suited for wood bonding<sup>21</sup>. Caesar reacted 0.25 to 2.0 per cent of potassium bichromate and 1 per cent lime on cassava or tapioca flour to obtain a strong adhesive<sup>22</sup>. Starch modified with finely divided clay and zinc oxide was found by Bahr to be suitable to the protecting of enamelled surfaces after it was deposited on a paper surface<sup>23</sup>.

Pierson combined a dry powdered starch, oxidizer, and urea to form an adhesive, the urea serving as a liquefying agent, and reducing the amount of oxidizer required<sup>24</sup>. The urea also retarded the rate of water evaporation from the glue after application, serving as a stabilizer in this capacity. Bauer added a small amount of acid to the starch-urea adhesive to stabilize it against decomposition of urea<sup>25</sup>. Shoals hydrolyzed starch in the conventional manner, adding borax and sodium hydroxide during hydrolysis. To this was added rubber latex which was slowly stirred into combination with the starch to form an adhesive product<sup>26</sup>. Pierson prepared a starch adhesive composition following the practice of some of the proteins, by including a small amount of dry copper sulfate<sup>27</sup>. Added to water, the cassava starch and a small amount of copper sulfate in a ratio of 2.5 starch to 1 of water (with 3 per cent NaOH), when heated to 65° and stirred for 1 to 2 hours, formed an adhesive of 44,000 to 48,000 poises viscosity.

Schrauth claimed that the addition of  $\frac{1}{2}$  to 5 per cent of higher alcohols (8 or more carbon atoms in the molecule) or sulfates or sulfonates of these alcohols improved the quality of starch adhesives<sup>28</sup>. Especially suited are lauryl, cetyl, stearyl, oleyl and ricinoleyl alcohols. Improvements are noted in the spreading and penetrating qualities and the adhesive strength. An effective combination is noted in equal parts of naphthol and oleyl alcohol sulfonate.

Bauer developed adhesives from starch and dextrans for application to the manufacture of paper products, in particular corrugated paper boxes, for which the sodium silicate adhesives have predominated for years. His developments covered an aqueous suspension of starch in a gelatinized starch medium. The suspended starch is gelatinized by a special machine which applies sufficient heat to develop the adhesive *in situ* as the paper is bonded<sup>29</sup>. Bauer indicated a preference of not more than 2.5 parts of water to 1 of total solids in the development of the corrugated paperboard adhesive. In further improvements, Maxwell included a salt of deacetylated chitin with unhydrolyzed starch to form a quick-setting adhesive which could be efficiently used on a board machine<sup>30</sup>. Champion and Denham developed starch adhesives for laminating paper, using largely enzyme-converted starch, in combination with some unconverted starch. Properties were controlled by maintaining a balance between the enzyme-liquefied starch and the unconverted portion, which was added after heating the first portion above the gelatinizing temperature<sup>31</sup>. Fenn specified more than 55 per cent of enzyme-converted starch and less than 45 per cent of raw starch with a small amount of sodium chloride or calcium chloride in developing an adhesive<sup>32</sup>.

Kreimeir and Maxwell alkylated starch in the presence of an alkali to prepare some adhesives. Ethyl or methyl sulfate (0.02 to 0.75 mole per  $C_6H_{10}O_5$ ) were reacted upon a water suspension of starch<sup>33</sup>. The sodium hydroxide was added slowly so that there was no large excess of unreacted alkali at any time, until the starch was alkylated. Starch esters may also play a prominent role in the field of adhesives. Caesar dispersed starch in phosphoric acid and then acetylated the structure to prepare some starch esters, while Smith and Treadway esterified starch swollen in formic acid<sup>34</sup>. Considerable work has been done in examining the solubility of starch triacetate, and results have been reported on the effect of 105 plasticizers at 25°, 100°, and 180°<sup>35</sup>. Nitration of starches in chloroform with the aid of nitrogen peroxides has also been carried out<sup>35a</sup>. There was a minimum degradation of starch molecule. Starch containing not more than 20% water was acetylated with acetic anhydride and acetic acid by Treadway<sup>35b</sup>.

In examining the mechanical properties of starch derivatives, Whistler and Hilbert fractionated fat free corn starch with butanol to separate the amylopectin from the amylose. The amylose and amylopectin were acetylated independently and properties of the triacetate films were determined. The amylose triacetate films proved to be greatly superior mechanically and ability to blend with plasticizers, as compared to amylopectin triacetate. The brittleness of starch films is attributed to the highly branched amylopectin portion<sup>36</sup>. Selective solvents of nitroethane, 1-nitropropane, and 2-nitropropane were employed to separate amylose from amylopectin. As good yields were obtained with these solvents as with butanol<sup>37</sup>.

The water resistance of vegetable glues suffers in comparison with other types, limiting many of the articles bonded with these materials to interior use. Osgood and Peterson attempted to develop a waterproof starch-base adhesive, employing formaldehyde or formaldehyde reaction products (as urea-formaldehyde) in conjunction with unconverted starch<sup>38</sup>. The addition of 15 per cent of urea resin (based on solids) to starch adhesives greatly improved the weatherproofing qualities of corrugated paper containers<sup>39,39a</sup>. To prepare the unconverted starch for the glue spreader, Osgood and Peterson suggested in one method the addition of an equal weight of formaldehyde solution (40 per cent in water) which forms a thick paste with the starch after standing at room temperature for several hours. Unconverted starch may also be prevented from separating out in the glue spreader by casein glue, sulfite concentrated liquors, animal glue or others. The pH of their adhesives, on the slightly acid side, did not stain the wood veneers when bonding with heat and pressure. Preference was also shown for the addition of 15 per cent of zinc chloride and 10 per cent of zinc sulfate based upon the weight of the starch. Acid salts of amides plus starch will rapidly form a paste which is readily thinned and capable of large amounts of solids. These compositions have proven good for textile and paper sizing<sup>40</sup>.

Ward also prepared a low viscosity starch by dissolving starch in trimethyl benzyl ammonium hydroxide or dimethyl dibenzyl ammonium hydroxide<sup>41</sup>. A water-soluble starch sizing was developed by Bierly by reacting starch, lactic acid, and sodium chlorate at 110°. Sizings were applicable to rayon threads and other fabrics<sup>42</sup>. As a laminating medium for asphalt-impregnated plyboard, ungelatinized starch in a gelatinous carrier was combined with 0.5 to 10 per cent of an emulsified asphalt (containing 58 to 62 per cent of asphalt) and applied as an adhesive<sup>43</sup>. This same principle will permit the combination of an aqueous suspension of starch with emulsions of various synthetic resins, and as our understanding

of the latter technique improves, one may expect further activities in the field of laminating resins and adhesives combining the starches with other high polymers.

A combination of cassava starch and sodium silicate will yield an inexpensive and stable formula. Braude<sup>4</sup> describes a typical combination, which is itemized below. The starch is suspended in water and sodium hydroxide is added at room temperature. When the mass is clear, the sodium silicate is added and followed by borax dissolved in water. The adhesive is neutralized with a dilute mineral acid solution:

Cassava starch	130
Water	160
Sodium hydroxide (36° Bé)	33
Water	28.0
Sodium silicate (35° Bé)	43.0
Borax	0.1
Water	13.0
Hydrochloric acid (22° Bé)	35.0
Water	17.0

Various compositions have been worked into starch adhesives involving salts which increase the density and reduce the tendency to gelatinize. Others improve the tendency of the starch granules to swell on contact with water. It is generally recognized that the less the starch has been converted, the greater its ultimate adhesive strength, though some modification is practiced to aid the method of application.

Gardner prepared a stable starch adhesive by heating an organic hydroxy compound (32 to 110 mol. wt.) with amylaceous material under acidic conditions in presence of insufficient moisture to cause gelatinization until the product exhibits improved adhesive strength<sup>44</sup>. By roasting starch above 300°F. in presence of formaldehyde, a product was obtained which would form short, soft pastes without granular disintegration<sup>44a</sup>.

In reporting on the serviceability of glue joints prepared with various adhesives, Brouse revealed a comprehensive series of tests which give a good picture of the relationship of animal and vegetable glues to the protein types, and the blood albumin-paraformaldehyde adhesives<sup>45</sup>. Synthetic-resin adhesives, which are noted as superior to all of these types to the conditions of exposure, were not included in these investigations which commenced at a time the synthetics had not attained commercial importance in this country. The investigation was directed to an evaluation of the strength of plywood prepared from  $\frac{1}{16}$  inch yellow birch veneer. From the curves reproduced below from Brouse's paper, it is evident that the animal and vegetable glues are not safe at humidities of 80 per cent and higher, and the proteins at 90 per cent relative humidity. The test cycles included the following:

Data on Exposure Tests (Brouse<sup>40</sup>).

Test No.	Time of Exposure Cycle	First Stage		Second Stage	
		Time (days)	R. H. (%)	Time (days)	R. H. (%)
1	continuous		30		30
2	alternating	14	60	14	30
3	"	14	80	14	30
4	"	14	90	14	30
5	"	14	97	14	30
6	"	Soak in water 2 days		12	30

The vegetable glue used in these tests consisted of 100 parts of processed starch, 3 parts of sodium hydroxide, and 225 parts of water. The comparative results taken from Brouse's paper are reproduced in the Figures 38, 39, and 40.

## CYCLIC TESTS—HIGH HUMIDITY vs LOW HUMIDITY

(Data by Brouse)

Relative humidity (per cent)

No. 1. 30-30. No. 4. 90-30.

No. 2. 60-30. No. 5. 97-30.

No. 3. 80-30. No. 6. soak.

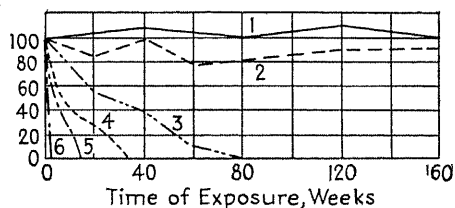


Figure 38.

Durability of animal and vegetable glues.

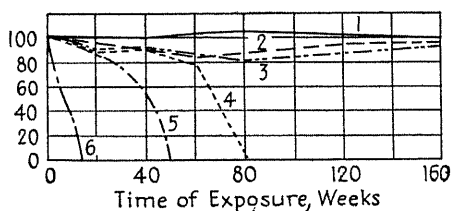


Figure 39.

Durability of casein glues.

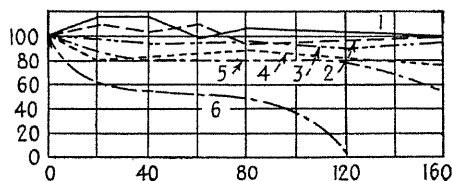


Figure 40.

Durability of blood albumen plus  $(\text{CH}_2\text{O})_x$ .

## Dextrin Adhesives

The more soluble dextrans, prepared by roasting the starch or treating starch with acid, followed by drying and roasting, have served as the basis

for numerous adhesives. They do not have as good strength as the starch adhesives, though they are more soluble and set more rapidly. Many of the commercial adhesives now in use are based upon dextrans or at least partially converted starch. The dextrans are sometimes classified according to their color and their degree of cold water solubility. White dextrans are soluble to the extent of 25 to 75 per cent in cold water; slightly colored dextrans are about 97 per cent soluble in cold water; while more highly colored varieties are completely soluble. They are generally sold in powdered form and should be stored dry and away from vermin. The characteristics of the dextrans are dependent upon the origin of the starch from which they were prepared and the technique of the conversion. The percentage of glucose formed is usually held to a minimum because glucose tends to increase hygroscopicity and decrease adhesiveness.

Dextrans may be slightly on the acid side, and though this forms a clearer solution, better adhesive qualities are developed if alkali is added. Borax is also an important additive which increases the consistency of the adhesive solution and improves its stability. It is usually added before the alkali is introduced. A typical alkaline dextrin adhesive paste described by Dulac comprises the following:

Water	500
Dextrin	390
Borax	46
Sodium hydroxide (30° Bé)	6
Sodium bisulfite	4

The function of the sodium bisulfite is to mask the odor, act as a preservative, and bleach the material. The dextrin and one-half of the water are stirred until the lumps are eliminated and then the rest of the water is added and the mixture heated to 85°. Borax is added and dissolved, followed by the sodium hydroxide.

Radley described a quick-setting machine adhesive suited for sealing wrappers consisting of 40 parts of dextrin, 40 parts of borax and 50 parts of water. Sodium hydroxide, phenol, and Turkey red oil were added to the formula<sup>12</sup>. The latter component tends to plasticize the film and is not too hygroscopic.

A review of recent developments in dextrin adhesives will indicate some of the problems confronting these materials. Edson dextrinized starch in discrete particles, preserving the original starch cells. These were dispersible in water without the usual tendency to cohere<sup>46</sup>. Farber carried the process of dextrinization further, obtaining at least a partial conversion to polysaccharides, which on mixing with urea and with phthalic anhydride formed adhesive products<sup>47</sup>. It is possible that he attempted some

condensation reaction between the polybasic acid and the polyhydric alcohols formed.

Various salts are combined with the dextrans as they are with the starch adhesives. Jones suspended corn dextrin in water with approximately  $\frac{1}{2}$  its weight of anhydrous calcium chloride. The temperature was raised to 85° to obtain complete solution, which was then quickly cooled to make a permanent concentrate for adhesive base<sup>48</sup>. It will be observed that many of the later patents on dextrin adhesives are careful to note the percentage of soluble material present (or the percentage of unconverted starch)—data which were not always present for the dextrin adhesives described in earlier literature.

Wakeman developed a dextrin-base adhesive for adhering to oily surfaces. Tapioca dextrin (28 to 35 per cent soluble) and dextrose (under 3 per cent) were intimately mixed with borax and a hygroscopic agent<sup>49</sup>. Smith prepared a non-aqueous adhesive for sealing and labelling packages by fusing 45 per cent ammonium acetate with 55 per cent dextrin at 80 to 100° with agitation<sup>50</sup>.

Adams and Davidson coped with the problems of reducing discoloration on aging for the envelope adhesives. They pointed out that discoloration was due largely to reaction between degraded proteins present as sizing agents in the paper and reducing sugars formed in the paper adhesive. Their adhesives were designed for machine application and consisted of the following (<sup>51, 52</sup>):

Water	10-18 per cent
Partially dextrinized starch	50-62 per cent
Fluidifying agent	3-10 per cent

In one instance acetamide, propionamide, or butyramide served as a fluidifying agent, while in still another example, esters of carbamic acid were specified<sup>53</sup>.

Adhesives for gluing wood have been prepared from dextrans (70 to 95 per cent) and a melamine formaldehyde resin (5 to 30 per cent)<sup>54</sup>. These are mixed together in cold water, ammonium chloride being added as a hardening agent for the synthetic resin. Salisbury employed sucrose, converting it into invert syrup in making the adhesive. He also combined sucrose and dextrans in dry mixes, adding small percentage of salts<sup>55</sup>. As a back-seam gum for envelopes of transparent window seals on envelopes, partially converted starch and dextrin are combined with 20 to 50 per cent of urea plus a small amount of organic acid to counteract the ammonia formed on heating at the time of application<sup>56</sup>.

Employing a dextrin of 20 to 95 per cent solubility in water at 25°, Bauer prepared an adhesive suited to papers, fabrics, and gummed labels;

from 3 to 30 per cent of urea and 1 to 10 per cent of glycerol were included. Borax was added to the water for remoistening, rather than to the adhesive mix<sup>57</sup>. Fast setting qualities are exhibited in its application. Further amylaceous compositions entailing starch dextrin mixtures were prepared for envelope sealing and wallpaper hanging. One interesting remoistenable adhesive comprised partially dextrinized wheat starch of 1 to 5 per cent water-solubility, urea and sodium acetate (20 to 45 per cent of total solids) and water<sup>58</sup>. Among other novel features of this group of patents was the use of slightly chlorinated starch as a raw ingredient of adhesive manufacture. As a plasticizer for remoistenable starch adhesives, sodium or potassium thiocyanate has been mentioned<sup>59</sup>.

A mixture of 90 per cent of comminuted dextrin and 10 per cent of granular dextrin has been described as the basis for adhesive products<sup>60</sup>. Edson developed some interesting dextrin-type adhesives for gummed tapes, labels, and stickers. For best properties he preferred a dextrin content of 10 to 20 per cent and water solubility at 25° of 30 to 50 per cent. Starch conversion products required 5 to 25 per cent of urea, the larger amount of urea for bases with the smallest dextrin content. Alkaline metal halides and alkaline-earth metal halides were recommended as good adhesive activators in combination with urea<sup>61</sup>. In still another technique applicable to gummed labels, Eiseman discloses the application of starch to the desired surface, followed by heat conversion to an adhesive film<sup>62</sup>.

Dextrins are also mixed with sodium silicate to form adhesive products. Bennett describes one of this character<sup>63</sup>, the dextrins first forming a homogeneous solution before other agents are added:

Water	90
White dextrin	30
Yellow dextrin	100
Glucose	20
Sodium silicate (38-40° Bé)	25
Sodium bisulfite (36-40° Bé)	50

Dulac describes a dextrin-type adhesive incorporating formaldehyde<sup>11</sup>. Good water solubility and flexibility feature this adhesive, which is applicable to gummed labels:

Water	600
Extra-soluble dextrin	400
Turkey red oil (90%)	0.4
Formaldehyde (30%)	120
Gelatin	20
Glycerin	40

The gelatin is soaked in 100 parts of water over night and then heated to 80° with stirring as the glycerin is slowly added. After the dextrin has

been dispersed in water the gelatin solution is stirred into combination. Bennett also discusses a dextrin-base adhesive for cementing paper to metal foils. Aluminum sulfate and glycerin are the additives recommended for this formula.

### Natural Resin Adhesives

Various miscellaneous adhesives are derived from natural sources either as tree exudations or as resinous excrements from parasitic insects. In a few cases they have been employed for their own particular adhesive qualities, though more often they are added as modifiers for more costly synthetic resins or cellulose derivatives. These natural resins are often sticky in themselves and are definitely thermoplastic in nature. Their adhesive formulation generally involves solution in a suitable solvent before application.

In examining miscellaneous natural resin adhesives, we will select a few at random from patent literature to bring out distinguishing features. For example, Jenkins developed an adhesive for floor covering comprising 5 parts of manila gum dissolved in alcohol. To this was added 6 parts of plaster of paris<sup>64</sup>. As an adhesive for paper products, Wolfe employed adhesive agents from gum arabic, gum senegal, gum tragacanth, and shellac in conjunction with sodium hydroxide as a saponifying agent<sup>65</sup>. As a linoleum adhesive, Coleman employed concentrated molasses residue from the distillation of molasses which was then added to a finely divided clay and water. This formed a thermoplastic clay which was readily spreadable<sup>66</sup>. Jelutong gum and castor oil have been recommended for their adhesive properties<sup>67</sup>.

Various water-soluble gums are particularly valuable to the adhesives field. A number of these are derived from the exudations of the various kinds of acacias. Most notable of these is gum arabic, which is soluble in two or three times its weight of water. Gum arabic, usually sold in powdered form, is a safe, simple adhesive for miscellaneous paper products. In this group may be included gum senegal and gum ceresin which may be mixed with gum arabic. Various mucilages have been prepared from gum tragacanth and gum bassora, which are not as soluble in water as gum arabic. Gum tragacanth is generally employed as a thickening or sizing agent for other adhesive products.

Copal resins are well known in the varnish industry, particularly the harder fossilized deposits; softer varieties are tapped from trees. Blended with about 20 per cent of castor oil they form an adhesive recommended for tapes<sup>68</sup>. A waterproof adhesive is prepared by melting together a small amount of gum elemi and castor oil<sup>69</sup>. Another adhesive suggested as a tin can sealer consists of the following<sup>69</sup>:

Soft manila gum	150
Gum elemi	5
Ether	100
Denatured alcohol	55

The following adhesive formulation has been recommended for gluing cellophane<sup>70</sup>:

Gum arabic	16.5
Glycerin	29.5
Water	49.5
Formaldehyde (40%)	4.5

The natural resins are frequently mentioned in connection with cements for floor coverings—an ideal type of application where their thermoplastic qualities would be an asset, and where the effects of creep would not be as significant as in semi-structural applications. Manila gum dissolved in denatured alcohol and a low cost aromatic solvent (for example, Union # 8) is augmented with fuller's earth for application to underside of floor coverings<sup>69</sup>. In still another example of this type, manila gum (6 to 10 parts) is blended with air-blown linseed oil (27 to 35 parts), and the two dissolved in denatured alcohol. Bentonite clay is introduced to reduce flow and improve spreadability<sup>71</sup>. Adams expresses preference for an acaroid resin dissolved in denatured alcohol and mixed with slate flour for application to hard surfaced floor coverings<sup>72</sup>. Bohne employed pectin substances and sorbitol as temporary adhesives for some of his dental work<sup>73</sup>.

Rosin and rosin derivatives have played important roles in the field of adhesives. For example, Ware specified rosin plasticized with no more than an equal weight of petrolatum and a volatile solvent for use as adhesive<sup>74</sup>. For moisture-proof cellophane the following rosin-base adhesive has been recommended<sup>75</sup>:

G-rosin	70-29
Venetian turpentine	29-70
Diethylene glycol ether	1-20%

Abietyl alcohol, derived from rosin, when esterified with methacrylyl chloride and tung oil acids, forms products useful as adhesives, as in the manufacture of safety glass<sup>76</sup>. Considerable interest has been shown in the gasoline-insoluble pine wood resin fraction, obtained by extracting resinous wood with coal-tar hydrocarbons and treating the extract with gasoline. The exact chemical nature has not been identified, though the product is called "Vinsol". It has been used as a low-cost extender for phenol-formaldehyde resin binders, though it has also stood on its own merits as a core binder<sup>77</sup>. This resin has also been employed industrially

in the manufacture of tubes of cellulosic materials previously impregnated and bonded with this material<sup>78</sup>. Another application of "Vinsol" which may be noted is its use in small percentages in Portland cement, as an air-entraining medium. ASTM specifications allow 0.025 to 0.045 per cent "Vinsol" by weight of the cement<sup>79</sup>.

An oxidized mixture of polymerized rosin and drying oil has been used as a linoleum binder<sup>80</sup>. Casein, animal glues, or starch are modified with triethylene glycol or glycol ester of rosin acid having a melting point of 25–80°<sup>81</sup>. An electrical insulating tape characterized by good insulation resistance and high moisture resistance employs an adhesive of 20 to 65 per cent of polymerized rosin, 30 to 70 per cent of a wax-like material, and 5 to 35 per cent of plasticizer for the polymerized rosin<sup>82</sup>. The methyl ester of abietic acid ("Abalyn") and the hydrogenated methyl ester of abietic acid ("Hercolyn") are well known as liquid plasticizing agents in various adhesive formulas. Additional rosin derivatives well known in the adhesives and coating field are: diethylene glycol di-abietate ("Flexalyn"), pentaerythritol abietate ("Pentalyn"), and a higher melting point pentaerythritol abietate resin ("Pentalyn-G"). "Flexalyn" is compatible with a wide variety of starches, casein, glues, and waxes. "Pentalyn" A and H are particularly applicable as tackifying resins based on GR-S and neoprene synthetic rubbers. Their high resistance to oxidation insures good tack retention and color stability. They are added to latex adhesives as an oil-in-water emulsion of 40 to 50 per cent solids.

"Hercolyn" and "Abalyn" have been recommended for addition to water-soluble film-forming materials such as starch, casein, and animal glue, forming stable emulsions which possess good adhesion and flexibility over a wide range of humidities. "Abalyn" is capable of undergoing reactions typical of the molecules containing conjugated double bonds, including the Diels-Alder synthesis with maleic anhydride. Films of this material slowly oxidize in the air. "Abalyn" may be emulsified by a slight excess of water containing 5 to 10 per cent of sulfonated castor oil. Both "Hercolyn" and "Abalyn" possess a high degree of wetability for various surfaces, particularly cellulosic fibers and metal surfaces. "Hercolyn" has been particularly recommended for combination with nitrocellulose, ethylcellulose, rubber, cyclized rubber, chlorinated rubber, and polyvinyl chloride-acetate adhesives<sup>83</sup>. The writer has also found these esters effective plasticizers for coumarone-indene resins; it is especially effective in pressure-sensitive adhesive formulations. The viscosity of these liquid esters are 2800 to 3400 centipoises at 25°, with boiling points in the neighborhood of 365°.

Mono-, di-, and triethylene glycol esters of *hydrogenated rosin* ("Staybelite" esters) are essentially non-oxidizing and are characterized by good

tack and adhesion. They range in softening point from free-flowing at 84° to a viscous liquid at room temperature. They find their widest use in the formulation of rubber and ethylcellulose adhesives. Approximately equal parts of triethylene glycol ester of hydrogenated rosin and high-viscosity ethylcellulose form a strong adhesive composition. These esters have also shown complete compatibility with urea-formaldehyde resins, adding gloss and adhesion. The compatibility of these esters with asphalt indicates their use in certain laminating adhesives.

Among other esters of rosin which are of promise in the adhesive field are the glycol esters ("Flexalyn"), which are used extensively in starch back sizing compositions for woven textile products. They improve flexibility and add toughness. Other rosin esters, such as glycerol ester of rosin (ester gum), long known in the field of surface coatings, have attractive tackifying properties for various adhesives. Various glycol esters of polymerized rosin ("Poly-pale Esters") function both as resins and tackifiers and are to be considered in adhesive developments. "Poly-pale" esters in some cases may be used to replace ester gum. A number of these glycol esters of rosin and rosin derivatives show promise in hot-melt formulations because of their relatively low softening points. In the following table some of the more important derivatives of rosin are summarized, which are of potential interest to the adhesives field<sup>84</sup>:

Rosin Derivatives	Softening Point (°C)	Boiling Point (°C)	Trade Name
Wood rosin			
Glycerol ester of wood rosin			Ester gum
Ethylene glycol ester of wood rosin	55°		"Flexalyn C"
Diethylene glycol ester of wood rosin	42°		"Flexalyn"
Methyl ester of wood rosin		360-365°	"Abalyn"
Hydrogenated methyl ester of wood rosin		365-370°	"Hercolyn"
Pentaerythritol ester of wood rosin	109-115°		"Pentalyn"
Hydroabietyl alcohol	33°		"Hydrolyn"
Hydrogenated wood rosin			
Ethylene glycol ester of wood rosin	55°		"Staybelite-1"
Diethylene glycol ester of wood rosin	38°		"Staybelite-2"
Triethylene glycol ester of wood rosin			"Staybelite-3"
Polymerized rosin			
Ethylene glycol ester of wood rosin	79°		"Poly-pale-1"
Diethylene glycol ester of wood rosin	60°		"Poly-pale-2"
Triethylene glycol ester of wood rosin	45°		"Poly-pale-3"
Gasoline-insoluble fraction of rosin	110-120°		"Vinsol"

In this discussion of rosin derivatives which appear interesting in the adhesives field, the fact that rosin by itself has long served useful adhesive

purposes is not to be overlooked. An adhesive for glass as comprised of rosin (7.5 parts) and Congo resin (2.5 parts) has been described<sup>9</sup>. This adhesive is used as a hot melt in the absence of solvents. Other hot melt adhesives can be prepared by adding 3 to 10 per cent of film-forming ethyl-cellulose or cyclized rubber to glycol esters of wood rosin. A recommended starting point for a pressure-sensitive adhesive comprises the following<sup>85</sup>:

Nitrocellulose	35
Plasticizer	25
Glycol ester of wood rosin	45

The extensive role of rosin in the processing of rubber adhesives has already been discussed in the chapter on rubber adhesives. In these and many other adhesive roles, rosin and rosin derivatives will fulfill important functions.

### Shellac Adhesives

Another naturally occurring resin from which has been prepared a number of interesting adhesives is shellac, which is a resinous excretion from a parasitic insect that infests certain fig trees in India. There are grades of various degrees of purity and color, the bleached varieties being preferred for the surface coating industry. Shellac is readily soluble in ethyl or methyl alcohol, forming a solution from which it may readily be applied. It also enjoys a large market as a binding agent for phonograph records, affording a hard surface and good fidelity for reproduction of mold details. Commercially it is usually available in flake form suitable for compounding.

Perhaps the earliest use of shellac as an adhesive may have been in the manufacture of sealing waxes for envelopes, which could be softened when heated and embossed with some mark or seal. In its formulation into adhesives, shellac is generally blended with other resins to give it various degrees of hardness. A typical adhesive for metal to metal which has been suggested comprises<sup>69</sup>:

Bleached shellac	100
Sandarac gum	40
Castor oil	15
Denatured alcohol	430

Ordinary sealing waxes are prepared by mixing together and heating to a thin melt 4.5 parts of shellac with 1.5 parts of rosin and 0.5 part of turpentine. To this may be added barytes (3.5 parts) and 0.5 part of a red vermilion pigment. A very useful laboratory cement for joining pieces of apparatus together is the "De Khotinsky Cement", prepared from shel-

lac. Containing no volatiles and applied by hot melt at 150°, it affords remarkably strong bonds between non-porous surfaces. One method of preparing it is to blend 70 parts of a light brown orange shellac with 30 parts of heated pine tar, though an alkali-soluble beechwood creosote containing 25 per cent of terpineol as a plasticizer is sometimes considered to yield a superior product with shellac<sup>70</sup>.

In reviewing the art of linoleum adhesives, Ohl claimed that the first successful one developed was a shellac-copal gum preparation<sup>86</sup>. Mica splints have long been cemented into larger more usable sheets with the aid of shellac solutions and zinc oxide. After removal of solvent they are pressed at 200 psi at 125 to 265° to form an insoluble reaction product<sup>87</sup>. A small percentage of ethylcellulose (5 to 20 per cent) blended with shellac is reported as assisting in the bonding of mica flakes<sup>88</sup>. Hill introduced some refinements in the preparation of laminated mica with the aid of a shellac binder. Sheets measuring 0.005" to 0.020" were prepared and placed under vacuum at 20 to 80° for 4 to 20 hours. These were then laminated under heat and pressure<sup>89</sup>.

In a typical label application Alden applied shellac to one surface from a volatile solvent; at the time of application, the label was remoistened with a solvent and plasticizer for the shellac<sup>90</sup>. Shellac derivatives have also received their share of attention. Gidvani described a number of interesting ethers and ether-esters of shellac and their polymerization<sup>91</sup>. Ethylene glycol ether of shellac appeared to have much promise.

Among the products of shellac hydrolysis by warming with 0.5*N* potassium hydroxide, aleuritic acid  $[(\text{CH}_2\text{OH} \cdot (\text{C}_2\text{H}_5) \cdot \text{CHOH} \cdot \text{CHOH} \cdot (\text{CH}_2)_7 \cdot \text{COOH})]$  appears as a component whose constitution has been definitely established. This should prove to be an exceedingly interesting material for further reactions because of the presence of hydroxyl and carboxyl groups on the same molecule. The India Lac Research Institute recommends a transparent adhesive for laminating safety glass and other articles from a reaction product of aleuritic acid and phthalic anhydride<sup>92</sup>. Articles bonded with this adhesive may be cured at 80 to 90° for fifteen minutes. This same reference discusses the possibilities of using shellac modified with urea formaldehyde or melamine-formaldehyde as an adhesive in the manufacture of laminated boards. The presence of the synthetic resins augments the resistance of the shellac to heat and water.

Another modified shellac adhesive is prepared by refluxing 50 parts of formalin with 100 parts of shellac at 120°. To this is added 200 parts of alcohol, followed by further refluxing with 15 parts of urea. A plasticizer consisting of 10 parts of *p*-toluene ethyl sulfonamide improves the elasticity of the adhesive film<sup>92</sup>. One further cement for porcelain and china which may be mentioned is prepared from:

Shellac (bleached)	50
Mastic gum	35
Venetian turpentine	10
Zinc oxide	5

Shellac adhesives have proved their usefulness in bonding metal parts, ceramic parts, mica flakes, and non-porous materials. While they became quite scarce in this country during World War II, increasing attention is being paid to the various derivatives which may be prepared from these compounds.

### Asphalt or Bitumen-base Adhesives

One further group of adhesive materials which falls under the classification of natural resin adhesives, is that comprised of asphaltic or bitumen-base materials. Mention of them has been already made in connection with the development of certain specialty adhesives in the synthetic rubber field, though we shall now examine some of the adhesive qualities of these materials by themselves or in those compositions where they exist as a major component. Asphalts have been used as binding materials for a good many years. Occurring in various sources, the asphalts consist of many compounds and constituents obtained by various refining processes. Their major advantages are abundance and low cost. Definitions which have been proposed for the materials by the American Society of Testing Materials indicate their broad physical and chemical characteristics:

*"Bitumens:* Mixtures of hydrocarbons of natural or pyrogenous origin, or combinations of both, frequently accompanied by their non-metallic derivatives which may be gaseous, liquid, semi-solid, or solid, and which are completely soluble in carbon disulfide.

*"Asphalts:* Black to dark brown solid or semi-solid cementitious materials which gradually liquify when heated, in which the predominating constituents are bitumens, all of which occur in the solid or semi-solid form in nature or are obtained by refining petroleum, or which are combinations of the bitumens mentioned, with each other or with petroleum or derivatives thereof."

To these may be added asphalt emulsions prepared from steam-refined oil asphalt or natural asphalt; these are also of potential interest in the adhesive field. Asphalts are usually considered to be a dispersion of a solid material called asphaltene in an oily medium called petrolene. The asphaltenes are generally considered to be those components of asphalt which are insoluble in low-boiling paraffinic hydrocarbon solvents<sup>28</sup>.

There are three chief types of bituminous base adhesive materials:

- (1) Those comprising a bituminous base, volatile solvent, plus modifying resins, with or without drying oils.
- (2) A bituminous base with a large percentage of drying oils.

- (3) Emulsified asphalt base plus resin or rubber compounds dissolved in water or a latex form.

A review of typical adhesives formulated around a bituminous base reveals certain specialized uses, such as binders for mineral aggregates or adhesives for felt or felt-metal assemblies. Such compositions reflect the characteristics of the binding material, which in this case are quite susceptible to changes in temperature. Farrell proposed refined asphalt (80 parts), an oxidized mineral oil (16 parts), and rubber (3 parts) dissolved in an appropriate solvent as an adhesive for paper or wood veneers<sup>94</sup>. As an example of the type (2) listed above, Lemerle employed oxidized drying oils plus only 4 per cent of bitumen as an adhesive for waterproof abrasive products<sup>95</sup>. As an adhesive McLaurin employed an aqueous emulsion of asphalt as a major component and an animal glue, the dry weight of which was at least 10 per cent of the asphalt<sup>96</sup>. It has been reported that binders with high adhesive power are obtained by adding lead cresolate or phenolate to the bitumen<sup>97</sup>. An improved inexpensive adhesive which may be set at high temperatures was prepared for the purpose of bonding felt pads to metal panels. Proportions were as follows<sup>98</sup>:

Emulsified asphalt	12
Sodium silicate (40° Bé)	60
Clay (325 mesh)	28

Another heat-setting asphalt binder for cementing felt to car bodies which may be set from 100° to 165°, was sprayed or brushed into position. It was prepared as follows<sup>99</sup>:

Equal weights of asphalt and coumarone-indene or asphalt low in asphaltenes	40-45%
Soap emulsifier	0.8-1.2%
Clay (inhibits flow under heat)	1.3%
Rubber latex (increases bonding strength)	6-9%

As a binder for abrasive alumina and metal carbides for abrasive paper and cloth, Richter developed an emulsified asphalt binder with low brushing viscosity<sup>100</sup>. Asphalt (87 parts) was emulsified with 9 parts of stearic acid, 4 parts of triethanolamine, and 400 parts of water. The water was heated, emulsifying agents added, the asphalt melted and stirred vigorously. In another example of this same nature, Mack specified 0.5 to 5.0 per cent of an ester of a higher fatty acid and siliceous mineral aggregates<sup>101</sup>. In making friction facings for brake linings, Kirkshbraun employed a bituminous binder, glue or casein, clay, and asbestos fiber<sup>102</sup>.

A hot-melt adhesive for manufacture of paper containers was prepared from 30 parts of bitumen, 4 parts of linseed or tung oil, and 15 parts of

petrolatum<sup>103</sup>. Textiles and paper products have for a long time been waterproofed with solutions of bitumen (gilsonite), petroleum jelly, wool fat, and a drying oil<sup>104</sup>. Wardrell<sup>105</sup> as well as Adams<sup>106</sup>, and Abraham<sup>107</sup>, discussed roofing materials impregnated and bonded with bituminous base materials. Sealing tapes have been manufactured from asphalt blended with cyclized rubber or polyvinyl acetate<sup>107a</sup>.

Hirsch prepared an adhesive paste involving several components, among which were coal tar, congo gum, and urea, followed by the addition of casein and animal glue in ammonium hydroxide<sup>108</sup>. Wood plies have been laminated together with the aid of oxidized petroleum asphalt (m.p. at least 105°) 5 to 25 per cent of petroleum wax, and 10 to 35 per cent of a compatible resinous material such as wood rosin or a hydrocarbon resin from petroleum and coal tar<sup>109</sup>. Bituminous base cements have also provided a good measure of sound-deadening benefits, as pointed out by Marc<sup>110</sup>. Using two air-blown asphalts from petroleum residues (one refined and uncracked, the other cracked), he combined 35 to 55 per cent of asbestos fiber and a fine granular material, dissolving the entire mass in a petroleum solvent before application.

Of course one of the most important and largest uses for asphalt is in paving constructions and a tremendous amount of work has been covered in studying the problems of using them as binders for various aggregates. The American Society of Testing Materials has prepared a number of standards relating to the production and evaluation of materials suited to paving requirements. In addition there are various specifications for the employment of asphalt mastics in waterproofing. A typical one combining an asphalt cement, mineral filler, and mineral aggregate employs an asphalt with a softening point of 54 to 65° by the ring and ball method with a penetration at 25° of 0.2 to 0.4 cm by an ASTM penetration needle<sup>111</sup>. Holmes evaluated the adhesive properties of asphalt, which in his particular tests were determined by its resistance to displacement by water<sup>112</sup>. Various test methods were evaluated and substances which improved adhesion discussed. Many additives have been suggested for improving adhesive properties of paving materials for mineral aggregates. Oleyl amine was suggested by Holmes<sup>113</sup>.

In an excellent summary of asphalt paving emulsions, Barth discussed the preparation and characteristics of various types of asphalt emulsions, of the asphalt-in-water type<sup>114</sup>. They were grouped into fast, medium, and slow-breaking types—significant to the mode of application in paving work. Outstanding applications besides paving included waterproof structural masonry, rot-proofing of lumber, and waterproofing and coating of fabrics and paper. Fundamental aspects of storage stability and relationships between interfacial tension and limits of stability are pointed out.

Interfacial tension decreases with an increase in pH falling off rapidly after a pH of 10. The average size of the dispersed particle attains a minimum of about 2.1 microns diameter at a pH of 11.6 to 11.9 for Panuco (Mexican) asphalt<sup>114</sup>. Mayfield developed stable asphalt emulsions by using as a dispersing agent a saponified resinous material from rosin or "Vinsol" and methylcellulose, 0.01 to 0.1 per cent of the weight of emulsion<sup>115</sup>. Sealing tapes coated with blends of cyclized rubber or polyvinyl acetate and asphalt have been prepared<sup>116</sup>.

Among other binding applications for bituminous compounds are as cementing agents for explosive oxidizing agents employed in the manufacture of rocket propellants. Combined with various synthetic resins to control plasticity and temperature sensitivity, good property control is attained.

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## Chapter 12

### Animal Glues

Among the best known and earliest used adhesive materials are the glues prepared from animal sources. Their origin probably dates back to pre-historic time when man boiled game in water and found a gel left in the pot. Early uses by the Egyptians and Grecians are indicated in various records, which suggest that the art of preparing and applying animal glues was well known even at that time. The methods of preparing animal glue today are not radically different from those used for many hundreds of years. In the United States from 1926 to 1938, the annual production of animal glues averaged some 90 to 100 million pounds per year<sup>11</sup>.

Much has been written on the subject of animal glues and gelatin, and various formulas proposed for the gluing operations. For a more complete discussion of this subject matter, there are ample references<sup>1-5</sup>. Animal glues may refer to all glues prepared from the skins and bones of cattle, goats, sheep, horses, pigs, etc., though the commercial products are all derived from cattle, from which superior materials are obtained. In an earlier chapter another useful adhesive product obtained from cattle, namely blood albumin, was described in conjunction with the protein base adhesives.

Broadly the cattle glues are divided into three main classes: hide glue, extracted bone glue, and green bone glue. Hide glue is the strongest and most reliable of the three<sup>6</sup>, green bone glue the weakest in strength. The corium serves as the main source of hide glue; *collagen*, a proteinic compound is derived primarily from that region. Appropriate hide parts obtained from the butcher or tanner are specially processed, as described later, to give hide glue. Other parts of the animal also serve as raw materials for glue manufacture, though the characteristics of a glue are very much dependent upon the source and the method of manufacture. Most of the bone glue is produced as a by-product of meat packing or rendering of animal fats.

Glues are generally sold in cake, flake, ground, pearl and shredded form; however its physical appearance has no bearing on the strength and reliability of the glue joints. More than three-quarters of the domestic output of animal glue is sold in ground form, the remainder being largely

flake, with a small quantity of pearl. The form of the glue affects its ease of dispersion in water, the more readily soluble types being more finely divided.

Animal glues are employed widely in the woodworking industry, except where a water-resistant adhesive is required. High-grade glues (grades 9-12 in table on page 305) are used in laminating thick lumber, lower grades for veneer work. Before the synthetic resin adhesives were generally available, many important applications were entrusted to the animal glues. For example, Truax points out that they were used to glue airplane propellers together during the first World War, being the best and strongest glue available at that time<sup>7</sup>. Furthermore, they were easy to handle and sample for test purposes.

Because of the great variety in the grades of glue obtained from the different raw materials, several methods of classification have been proposed; the standards of the National Glue Manufacturers' Association are the most widely used<sup>8</sup>. The oldest system of classification of animal glues was that established by Peter Cooper in about 1844, ranging from the highest to the lowest grades. Today the classifications are based upon the relative order of viscosity and jelly strength. Another convenient method of classifying animal glues is presented in a government specification<sup>9</sup>. The grades adopted by the National Association of Glue Manufacturers in 1928 are tabulated on page 305.

While the top grades of glue will absorb 7 to 10 times their weight of water, the glues in the woodworking range absorb from 1.5 to 3 times their weight. However characteristics are more dependent upon the grade than the ratio of water to glue. Some of the animal glue films exhibit very high tensile strengths, and for a long time such glues were considered the best type for bonding wood<sup>10</sup>. Highest strengths are shown by glues derived from the hide. The major uses indicated for animal glue grades are as follows<sup>11</sup>:

*Hide Glue*—Furniture manufacture, surface-coated abrasives, sand paper, print rollers, sewing machine cases, clock cases, and flypaper.

*Extracted Bone Glue*—Trunks, fiber-board boxes and cardboard boxes, cartons, whips, and canes.

*Bone Glue (Packer's Glue)*—Gummed tape and paper, and paper cartons.

The various grades may be blended by the consumer to achieve certain results in applications of the glue to different bonding problems. In addition various natural resin adhesives and synthetic resin types may be blended with the animal glue to bring out various qualities. In a few of the many examples, we find gum arabic<sup>12</sup>, dextrin<sup>13</sup>, and a synthetic resin<sup>14</sup>.

Grades of Animal Glue

Grade	Jelly Strength (Grams)	Viscosity (Millipoises)	Typical Characteristics
1	18	22	Bone glue or blends with hide glue
2	36	25	"
3	58	30	"
4	82	36	"
5	108	44	"
6	135	52	"
7	164	61	General use in veneering for long assembly periods
8	192	69	"
9	222	77	"
10	251	85	General use in joints-short assembly
11	283	94	"
12	315	104	"
13	347	114	For use in warm and humid climates
14	379	125	"
15	411	136	"
16	444	149	
17	477	162	
18	512	177	

*Jelly Strength*—Weight in grams to imbed a plunger 12.7 mm diameter to a depth of 4 mm in a standard mixture.

*Viscosity*—Measured in a calibrated capillary type pipette.

The amount of swelling a glue undergoes in contact with water may be expected to vary with the pH, a minimum point being observed at 7.7 pH<sup>12</sup>.

**Manufacturing of Animal Glues.** The manufacturing processes of the different types of animal glues primarily vary in the initial treatment of the raw materials. In the manufacture of hide glue, the hide trimmings are soaked with lime to dissolve and remove albuminous and mucinous material, a process which may require from one to three months. The lime renders the bulk of the fat inactive by saponification, without appreciably reacting with the collagen (which is ultimately extracted for the glue)<sup>15</sup>. Control of concentration, temperature, time, and pressure is most important during the processing and conditioning of the raw materials. After an appropriate liming process, the alkali and other chemicals must be removed completely by washing with pure, clean water. Some manufacturers add a small amount of weak acid to neutralize the lime and re-

duce the washing period, which may extend over several weeks. Thorough cleansing is important and washing and kneading with pure water is necessary. When thoroughly washed and swollen, the stock is ready for extraction of the glue.

In the extraction of the glue, which is accomplished merely by the action of heat and water, the swollen hide glue is placed in an extraction kettle containing closed steam coils, and a low heat applied for several hours. As the extraction continues, the liquor is tested, and when there is 4 to 5 per cent of glue present, it is drawn off for subsequent processing. More water is added to the stock and the process repeated at a raised temperature. This procedure is followed for 4 or 5 runs, each time raising the temperature until the boiling point is reached. Best quality glues are obtained during the first extraction.

The next step in the manufacture of the glues is to remove much of the water from the liquors by evaporation under vacuum and a low temperature. The amount of water removed depends upon which of the extraction runs the liquor was removed from, each succeeding run being evaporated to a higher percentage of glue. After part of the water is evaporated, the liquor is cooled and run on to a wide long belt. This is known as spreading and the glue then passes slowly through a refrigerated box. Upon emerging from this box, the glue has set to a jelly which is scraped off and dropped on wire covered racks. Slow and careful air drying is now applied to the various batches, which are finely "cracked" into flakes, ground or pulverized.

In the manufacture of extracted bone glue, the bones are crushed and fed to steel tanks where the grease is extracted with the aid of a solvent. After removal of solvent, the bones are tumbled in rotating drums with dilute acids to remove salts and then after washing are ready for the extraction process, similar to the one described for hide glue. Stronger acids may also be used to treat bones<sup>17</sup> at a pH under 5.0. The process for the manufacture of green bone glue is similar to this, except that the solvent extraction of grease is omitted<sup>11</sup>.

**Testing of Animal Glues.** All types of animal glue are thoroughly tested, graded, and classified. This is very important when considering the variations which exist among the raw materials and manufacturing processes, any one of which may affect the quality of the final product. Routine laboratory tests of animal glue include viscosity measurements, jelly strength, melting point (of jelly), moisture content, pH, appearance of foam, odor, per cent of grease, color, and keeping qualities. The ultimate adhesive qualities of the animal glues are closely related to the viscosity and jelly strength. These two tests are used for determining the grade of the glue, tabulation of which appeared earlier in this chapter.

*Viscosity.*<sup>8,9</sup> The standard procedure for determining viscosity is to place 13.2 grams of dry glue (calculate from apparent moisture content) into a wide mouth bottle 150 cc in capacity, with an inside diameter of 59 mm, and outside diameter of 66 mm, and an over-all height of 85 mm. To the glue shall be added a total of 106.8 grams of water, giving 11 per cent of solution based on the anhydrous glue. Mix with stirring rod and allow to stand for 4 hours at 10 to 15°. Bring to a temperature of 62° in a water bath at 70°, and determine the viscosity in a jacketed pipette viscosimeter calibrated in poises. The temperature of the glue solution at the time of measurement should be 60°.

*Jelly Strength.* The samples used for the viscosity test are placed in special containers and used for jelly strength determination. Samples are placed in a chamber or bath at  $10 \pm 0.1^\circ$  for 16 to 18 hours. A Bloom gelometer<sup>8</sup>, adjusted to give a 4 mm depression and deliver a load of 40 grams per second is applied to the surface of the jelly. Test must be completed within two minutes upon removal from the cooling chamber.

The usual acidity of the glue solution is within a pH of 5.5 to 7.5. Foaming is measured by vigorously stirring a portion of the viscosity sample at 60°, and after standing for 10 minutes not more than approximately 3 per cent of foam shall be present (measured volumetrically by eye).

When animal glues are to be employed in the bonding of wood, wood joint tests are desirable though it is generally recognized that for animal glues these are secondary to the viscosity and jelly strength tests. In a later chapter on testing of adhesives, the wood joint shear tests for wood will be described more fully. In testing animal glues, the wood blocks are generally conditioned before the application of glue, at 30 per cent relative humidity. After an overnight clamping they are returned to 30 per cent relative humidity for a seasoning period of one week before testing.

**Selection and Preparation of Animal Glues.** Typical end uses for animal glues of various grades have already been indicated in the table showing the standard grades. However, the selection of the correct grade does not guarantee good results unless proper care in application and close observance of the manufacturer's instructions are followed. To convert the dry glue into a liquid for woodworking for example, the glue and the water are both accurately weighed and the glue stirred slowly into pure cold water at 10 to 15° (never add water to the animal glue). After soaking for a couple of hours—about 2 hours for ground glue and about 6 for flake—the glue is melted by heating in a water- or steam-jacketed container, to a temperature of 60°. A good grade of hide glue will go into solution at a lower temperature, and it is imperative that care be exercised to prevent the glue solution from rising above this temperature, otherwise it will deteriorate. Clean glue pots are an asset. The amount of water to be

added depends upon the consistency required (determined by the method and extent of application) and the grade of animal glue used. The ratio of water to glue will usually be about 1.5 to 3 to one part of glue.

The animal glue requirements should be prepared for one day's run only, and new batches should not be added to old batches. Workrooms for glue application to wood are preferably maintained at 25 to 30°.

Sometimes the glues are bleached, as with sodium bisulfite or with sulfur dioxide. For the more alkaline glues, hydrogen peroxide is used, while some manufacturers use zinc dust and sodium bisulfite or sodium hydro-sulfite<sup>16, 18</sup>. The animal glues are not water-resistant and are considerably inferior to the synthetics in this respect, though initial strengths in bonding wood may be comparable. Deterioration caused by bacterial growths is also pronounced under highly humid conditions.

Liquid animal glues decompose rapidly unless a preservative such as formic acid, phenol, salicylic acid, benzaldehyde, etc. is used. The presence of dextrin and gum arabic in glue solutions will improve viscosity and inhibit gelatinization<sup>13</sup>. To improve the water resistance of the glue, certain chemicals or resin-forming ingredients may be added to the solution. Various tanning agents which are used with leather will also insolubilize the glue. Formaldehyde is frequently used, and about 1 per cent based on the dry weight of the glue may be added. While glue or gelatin treated in this manner may be rendered insoluble, urea may be added to render the glue soluble again<sup>19</sup>. Urea or biuret has a decided liquefying effect upon animal glue solutions. Ordinary glues gelatinize above room temperature requiring heat to liquefy. The relationship between the per cent of urea and the setting temperature is shown below<sup>20</sup>:

Per Cent Urea—Based on Bone Dry Glue	Setting Temperature
%	(°F.)
20	64
30	58
40	50
50	45

In a more recent specification a preference was expressed for 2.5 to 10 per cent of urea based on the dry animal glue. This percentage gave prompt remoistening and rapid resetting, but was insufficient to be hygroscopic. Calcium nitrate may be substituted for the urea<sup>21</sup>. The application of such formulas to gummed labels is indicated. In another woodworking glue, 100 parts of dry glue are added to 200 parts of water, and 8 parts of urea and 8 parts of glycerin, the two latter agents constituting flexibilizing agents<sup>22</sup>.

Glues suitable for pasting labels on tin cans, may be prepared from a mixture of starch, sodium silicate, and gelatin in the following proportions<sup>23</sup>:

Wheat starch	100 parts
Water	700 "
Gelatin	10 "
Sodium silicate	100 "
Turpentine	50 "

The starch and part of the water and gelatin and water are mixed separately and when both are dissolved they are combined followed by addition of the sodium silicate. A more water-resistant type of animal glue has been described by Browne<sup>24</sup>. In a typical test with 3-ply panels of  $\frac{1}{16}$  inch birch veneer, average shear strengths of 475 psi were obtained when dry and 165 psi after soaking in water for two days, the latter value being within the range exhibited by some protein glues. The proportions used were as follows:

Animal glue	100 parts (by weight)
Water	225 "
Oxalic acid	5.5 "
Paraformaldehyde	10 "

The animal glue is dissolved first, with gentle heating if necessary, before the addition of the other agents. The chemicals should be added at a temperature of 40 to 45°, and will remain fluid for 6 to 8 hours, after which the glue sets to an irreversible jelly. The water resistance develops slowly in the set glue, best performance being exhibited after two weeks of seasoning.

In a series of tests at Forest Products Laboratory a solution of caustic soda proved effective in reducing "starved" animal glue joints in woods. In a number of experiments with various species of wood, 51 per cent greater average shear strength was observed over those specimens untreated with caustic soda, and 97 per cent more wood failure<sup>25</sup>. Staining of the wood was encountered, however.

Improved water resistance is also obtained through combination of carbamides and aldehydes to the animal glue according to Geistlich<sup>26</sup>. Other wood adhesives were prepared by combining aqueous solutions of animal glue and urea or thiourea and formaldehyde<sup>27</sup>. Chromium and aluminum salts to the extent of 6.5 to 16 per cent are employed with animal glue at its iso-electric point of pH 4.7 to 4.9 to obtain a water-resistant formula<sup>28</sup>. Because of the rapid action of formaldehyde upon animal glue, hexamethylenetetramine may be added to a waterproof glue formula, yielding the aldehyde (which reacts with the gelatin) more slowly. Potassium alum, acetic acid, animal glue, followed by denatured alcohol are used in another waterproof formula<sup>28</sup>.

Another important use of animal glue in the adhesives field is as an

impregnating agent for the porous cellulosic backings of pressure-sensitive tapes. Drew combined 100 parts of animal glue with 400 of glycerine and 37 of calcium chloride for the manufacture of these tapes<sup>29</sup>. In still another application, Drew fused an equal mixture of glycerine and sugar and 750 parts of this glycerine-sugar combination were added to 250 parts of animal glue and 250 parts of water<sup>30</sup>. A tough, strong, flexible paper suitable for adhesive tape is produced with the paper fibers bonded quite firmly together. The side on which the adhesive may be applied is insolubilized first by a treatment with formaldehyde. Mechanical details for applying these agents have also been described in detail<sup>31</sup>.

Animal glue plasticized with glycerine or glucose has also been developed into a foil form for use as a plywood adhesive<sup>32</sup>. At least 70 per cent of bone glue was specified for this purpose. A water-soluble glue suited for labels and stamps has been prepared with the following combination<sup>33</sup>:

Trihydroxylethylamine abietate	25 parts
Polymerized terpenes	7.5 "
Animal glue	12.5 "
Potassium hydroxide	0.5 "
Water	85 "

Animal glues are also used as coatings for decalcomania transfers. Good adhesion to the lacquers is obtained without any bleeding action on the pigments. Dexheimer suggests the following combination for this purpose<sup>34</sup>:

Water	74 parts (by weight)
Hide glue	14.8 "
Glycerol	1.2 "
Monobutyl ether of ethylene glycols	10.0 "

This combination is good for roll coating. If the glycerol is too high the adhesive action is lost and if too low, the flexibility is impaired. Soybean lecithin has also been used for applications of animal glue to decalcomanias, aiding the spreading and acting as a plasticizer<sup>35</sup>. A flexible, non-hardening adhesive for paper was prepared from  $\frac{1}{2}$  acetic acid,  $\frac{1}{2}$  glue, and  $\frac{1}{10}$  glycerol<sup>36</sup>. An "ice-proof glue" for attaching paper labels to bottles is generally formulated with animal glue or protein, which is capable of gelling without modifying agents<sup>37</sup>. Lanolin is suggested as a means of reducing the water permeation through the labels. Sorbitol has been observed to hold more water than glycerol softened glues, at lower softener content and at lower humidities<sup>41</sup>.

In other miscellaneous animal glues of note, cashew nut shell liquid has been recommended in all proportions<sup>38</sup>, though dermatitis problems should be studied. Deacetylated chitin is recommended for increasing glue

viscosity. The adhesiveness of glues and gelatin has been improved through the additions of alcohols of higher molecular weight or sulfonation products thereof. For example, the sulfonate of lauryl or cetyl alcohol are cited<sup>40</sup>.

In an analysis by the U. S. Tariff Commission, the industrial distribution of animal glues has been broken down. Their results are reported as follows<sup>11</sup>:

Distribution of Animal Glues By Industry

Industry	Hide (%)	Extracted Bone (%)	Green Bone (%)
Furniture and woodwork	17.2	0.9	1.0
Abrasives	12.1	2.8	—
Matches	8.5	—	—
Automobiles	6.0	—	—
Print rollers	3.6	—	—
Boxes (paper and fiber)	1.4	1.0	12.9
Gummed tape and gummed paper	2.7	26.4	51.1
Paper, bags, wallpaper	7.6	16.3	1.1
Adhesives and glue manufactures	6.2	14.7	1.4
Kalsomine, paint, etc.	5.6	8.2	4.2
Jobbers	9.1	19.6	8.9
Miscellaneous	20.0	10.1	19.4
	100	100	100

### Fish Glues

A large number of household and commercial liquid glues are formulated on materials of marine origin—heads, bones, skins, and swimming bladders of fish stock. Like animal glue, fish glues are prepared by boiling properly prepared glue stock in hot water, followed by filtration and the evaporation to the desired consistency, and finally the addition of various deodorizing agents. They are marketed in barrels, bottles, cans, and tubes. Fish glues are used extensively in photoengraving, for gummed labels, and in inlay and repair work in woodworking.

Isinglass, which represents almost pure collagen, is obtained from the swimming bladders of the sturgeon and other fish. On soaking in cold water, isinglass swells slowly. Because of its higher price, it is generally adulterated with other ingredients. The raw materials for the manufacture of fish glues are obtained largely from cod, haddock, cusk, hake, and pollock—yielding a higher quality glue, particularly from the skin stocks. The fish glue industry in the United States dates back to 1874 when the first patent was granted for its manufacture<sup>11</sup>. In the years prior to 1931, the annual production averaged around 5 million pounds.

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## Chapter 13

### Sodium Silicate Adhesives

Sodium silicate is considerably different from the other adhesives examined so far in that it is inorganic in origin. It finds wide usage today in a number of specialized applications to paper and ceramic products. It is manufactured by the fusion of sand and sodium oxide to yield a soluble silicate, usually sold in a concentrated water solution. Sodium silicate products have been known for a good many years, though noteworthy commercial applications did not appear until the early part of this century.

Because of the abundance and availability of its raw materials, sodium silicate adhesives are low in cost. They are not as strong as animal or protein adhesives, but they give better strength than some starch and dextrin types. Unlike adhesives of animal origin they lack high tackiness; however, they demonstrate a large change of viscosity with change in the moisture content above a certain range. Characteristics and methods of applying the sodium silicate adhesive are dependent upon the ratio of sand and soda ash fused together in its manufacture. Exception is sometimes taken to its strong alkaline reaction, though this may not be a deterring factor in many of its uses.

Combinations of sodium silicates have already been examined in previous chapters, as for example, in the manufacture of water-resistant protein adhesives, the presence of sodium silicate gave prolonged working life. Combinations with water-soluble synthetic urea and melamine formaldehyde, starches, and animal glues have also been investigated and applied in several instances. By themselves, sodium silicate adhesives set rapidly, depending for their setting properties upon diffusion of water into a porous medium.

The practical range of silica ( $\text{SiO}_2$ ) to sodium oxide ( $\text{Na}_2\text{O}$ ) varies from a ratio of 2/1 to a ratio of 4/1. McFarlane lists the density for various practical concentrations of sodium silicate solutions, and for different  $\text{SiO}_2/\text{Na}_2\text{O}$  ratios. These are reproduced in part on page 314<sup>1</sup>.

In revealing rapid setting adhesives for the manufacture of laminated paper products, Vail and Baker presented a group of curves showing the relationships between viscosity and concentration of sodium silicate solutions for different ratios of  $\text{SiO}_2$  to sodium oxide<sup>2</sup>. It is apparent that with

Density of Sodium Silicate Solutions

Ratio $\text{SiO}_2/\text{Na}_2\text{O}$	% Sodium Silicate	Specific Gravity	°Twadell	°Baumé
2.0/1	55	1.70	140	60
2.5/1	47	1.56	112	52
2.9/1	45	1.50	100	48
3.3/1	40	1.42	84	43
3.95/1	33	1.30	60	33

only slight changes in water the viscosity may be greatly varied, though after passing the "knee" of the curve towards the axis, the viscosity change is very slow upon further additions of water. The commercial concentrations of sodium silicate are along the "knee" of the curve (see Figure 41) and when applied to paper stocks, as in a continuous pasting machine, the adhesive sets to a gel very rapidly upon the loss of a small amount of water. Vail and Baker recommended a silica sodium oxide ratio of 3.2 to 3.4/1 for best properties, within the optimum gravities of 37° to 41° Baumé. McFarlane recommended the following<sup>1</sup>:

For	Ratio	°Twadell
Paper tubes, spiral or straight wound	3.4/1	75-79
Sealing paper cartons (fast setting)	3.3-3.4/1	75-85
Sealing paper cartons (slow drying)	2.5-2.9/1	100-112

Sodium silicate adhesives are not usually recommended for labels because of the difficulty in washing them off. They are not generally used in woodworking, except for special examples, as in gluing up thin veneers. The animal, vegetable, and synthetic resins perform wood bonding more effectively. However, there have been various developments appearing from time to time in an effort to apply sodium silicate adhesives as bonding agents for wood structures. For example, Schleicher specified 16 parts of a sodium silicate solution to 1 of talc as an adhesive for veneer boxes<sup>3</sup>. Mixed with calcium, magnesium, and potassium carbonates and asbestos, sodium silicate solutions have been used as coatings for cements and woods<sup>4</sup>. Sodium silicate in combination with blood albumin has been developed as a plywood adhesive<sup>5</sup>. Sodium silicate plus water and animal glue have been also employed as wood adhesive<sup>6</sup>. In this example the proportion of water to animal glue was 4 to 8/1, and sufficient sodium silicate was added to maintain the adhesive properties of the glue when viscous at room temperature.

Sodium silicates have been employed for a large variety of binding requirements, ranging from metal powders for stereotype plates<sup>7</sup> to plaster board<sup>8</sup>. In the latter example, the plaster board was manufactured from sand (16), portland cement (24), woody fiber (96), water (50), sodium

silicate (100), and nitric acid (4 parts). Usually in such compositions asbestos is also present to increase the toughness of the finished product.

Vail describes a number of useful adhesive formulations employing sodium silicate<sup>9</sup>. He points out that the rosin sizing which imparts water resistance to certain cardboards, may be attacked by the more alkaline type of sodium silicate adhesive, reducing the water resistance. Generally it is practical to employ the silicate with the lowest  $\text{Na}_2\text{O}$  content which will dry at a speed consistent with the operation required<sup>9</sup>. In a typical

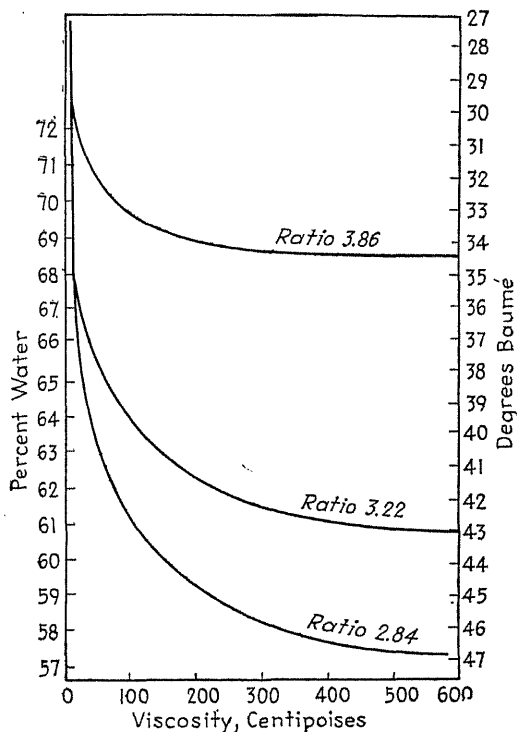


Figure 41.

Relation between viscosity and concentration of silicate of soda solution.

starch-sodium silicate adhesive, Vail described the following combination:

Starch	50 parts (by weight)
Water	100 "
Sodium silicate	50 "
$(\text{Na}_2\text{O}/3.34 \text{ SiO}_2)(\text{sp. gr. } 1.38)$	

The starch and water are stirred together and added to the sodium silicate solution, heating on a steam bath until the mixture clears. Accord-

ing to Vail, zinc and aluminum powders react sufficiently with sodium silicate ( $\text{Na}_2\text{O}/3.3\text{SiO}_2$ ) to develop a fair resistance to water within a few days. They can be used for filling defects in castings.

Small additions to sodium silicate may improve the adhesive qualities. For example, Veazey employs a small percentage of sodium or potassium chromate in sodium silicate adhesive compositions<sup>10</sup>. Larson modified sodium silicate adhesives through the addition of copper aminosulfate, claiming improved aging resistance when applied to chipboard. To 45.8 parts of copper aminosulfate (prepared from 14.4 blue vitriol, 16.5 water, and 14.9 aqueous ammonia) he added 200 parts of 42.5 Baumé sodium silicate ( $\text{SiO}_2/\text{Na}_2\text{O}-3.2/1$ ). An additional 14.6 parts of water are added to reduce the viscosity<sup>11</sup>. His claims cover 0.5 to 21.0 per cent of copper sulfate based upon sodium silicate solids. Other examples include modification with soyabean meal and tung oil. Zinc sulfate is also employed as a modifying agent for the sodium silicate adhesives by Larson. A typical combination includes:

Heptahydrate-zinc sulfate	10 parts
Water	40 "
Ammonium hydroxide (sp.gr. 0.9)	15 "
Sodium silicate	200 "
$(\text{Na}_2\text{O}/2.5 \text{ SiO}_2) (42.5 \text{ Baumé})$	

The zinc sulfate is dissolved in 20 parts of water and the ammonium hydroxide added. This combination is stirred into the sodium silicate which has been thinned down with additional water. Lettig claims the addition of a 12.5 per cent of copper sulfate solution to sodium silicate improves paperhangers' pastes<sup>12</sup>. Weygandt prepared an improved adhesive by heating sodium silicate with 0.1 to 1.0 per cent of zinc oxide in an autoclave at 150 to 180° until a homogeneous product was obtained on dissolution of the zinc oxide<sup>13</sup>.

In developing a silicate of soda adhesive for bonding grit to a flexible backing material, the tenacity of the adhesive is improved by body-forming agents of aluminum silicate, silica, or magnesium silicate<sup>14</sup>. Typical adhesive composition comprised the following components:

Base (low ratio sodium silicate)	350	parts (by weight)
Al or Mg silicate (body-forming agent)	100	"
Sulphonated castor oil	1½	"
Zinc oxide and calcium carbonate	0.7	"
Color agent (umber or sienna)	2.5	"

Additional body and shear strength are given to adhesives through the use of asbestos, as well as improved resistance to fire<sup>15</sup>. For improving the wetting qualities of sodium silicate adhesives various wetting agents have

been specified<sup>16</sup>. Included in these are up to 2 per cent of the following: sodium butylnaphthalene sulfonate, sulfonated castor oil, sodium ricinoleate, and oleic acid<sup>16</sup>. Advantages have also been observed through the inclusion of up to 3 per cent of an acetate radical in the sodium silicate solution<sup>17</sup>. Improved flexibility has been claimed for sodium silicate adhesives through the addition of a small percentage of coumarone-indene resin<sup>36</sup>.

Dulac claims a useful modified sodium silicate through the inclusion of finely powdered rosin, in the following proportions—5 parts of rosin to 100 parts of 36° Baumé sodium silicate<sup>18</sup>. This adhesive product is less alkaline and more viscous than one without the rosin. A strong adhesive for cementing felt on metal was prepared by Torri, using an emulsified asphalt in conjunction with sodium silicate<sup>19</sup>:

Sodium silicate	60 parts
Emulsified asphalt	12 “
Clay	28 “

### Sodium Silicate—Clay Compositions

Considerable interest has been shown towards adhesive formulations involving a finely divided clay and sodium silicate combination. Such combinations have found wide application to machine fabrication of laminated paper products, corrugated paper board, combined paper board, wallboard and similar products. Much effort has been directed towards the production of stable suspensions in an aqueous medium. Among the first to employ a finely divided clay was Carter, who suspended clay in sodium silicate (34° Baumé) in quantity of up to 80 per cent of its weight<sup>20</sup>. His purpose was to avoid excessive penetration of paper stock and retard drying time. The work of Thickens is also quite informative. He employed large amounts of clay to delay setting time, and develop wallboard and plyboard of many layers, possessing high rigidity. Using a non-refractory clay screened through 100 mesh, 92 parts were added to 100 parts of silicate of soda of 40° Baumé, followed by 15 parts of water<sup>21</sup>. Wood also cemented together various layers of paper with the aid of sodium silicate solutions<sup>22</sup>.

Vail and Baker, in developing adhesive compositions for corrugated board, used a  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio of 2.4 to 1. Hydrates of sodium metasilicate or sesquisilicate were not considered satisfactory<sup>23</sup>. In an improved process of deflocculating clay, Vail and Baker mixed in a dilute sodium silicate solution (0.1 to 10 per cent by weight)<sup>24</sup>. Additional silicate was then added to raise the viscosity to at least 20 centipoises and produce the adhesive product. In this manner smaller quantities of clay may be used with the adhesive. Bentonite clay is also indicated as a preferred

form in some cases. In the manufacture of adhesives suited to continuous machine fabrication, one of the claims of Vail and Baker<sup>2</sup> sums up the art in a satisfactory manner: "In the manufacture of quick-setting adhesives particularly adapted for high speed operations, the process which comprises mixing a fine-grained clay with water and with a soluble sodium silicate having a percentage ratio of  $\text{SiO}_2$  to  $\text{Na}_2\text{O}$  ranging from about 2.5/1 to 4/1 and so selecting the relative proportions and compositions of the ingredients as to produce an aqueous phase having a viscosity and gravity falling on the low viscosity portion of the knee of its viscosity-gravity curve and a finished adhesive containing not substantially more than about 20 per cent by weight of clay, with a viscosity range of about 50 to 500 centipoises."

A test was improvised to check the penetrating quality of the sodium silicate adhesive, using 40 cc of an adhesive upon a No. 40 Whatman filter paper in a long-stem analytical funnel, and determining the amount of clear sodium silicate which will filter through in 24 hours. If from 4 to 15 cc filtered through in 24 hours, the penetrating qualities of the adhesive were considered satisfactory for continuous pasting machines<sup>2</sup>. Boller, Lander, and Morehouse discussed the properties of adhesives used in the manufacture of corrugated fiberboard. The absorption of water into the paper determines the adhesive bond. From 10 to 15 seconds are required, and the adhesive must not flow away from the flutes of the corrugated fiberboard until they are assembled to the liner by pressing. From 16 to 30 pounds of sodium silicate (preferably 18 to 24) are employed per 1000 square feet, while a heavy liner (30 pt.) requires more adhesive. Production speeds are in excess of 300 feet per minute<sup>25</sup>.

In producing stable suspensions of china clay in sodium silicate, Boller dispersed clay in water and then admixed with sodium silicate in a colloid mill. Trisodium phosphate and borax were utilized as dispersing agents. The specific gravity did not exceed 41° Baumé<sup>26</sup>. In further refinements of sodium silicate-clay adhesives for corrugated fiberboard, Boller pointed out that the rheological properties of the clay-silicate mixtures determined its suitability as an adhesive. The adhesive must be readily applied from the rolls and have sufficient body to remain momentarily on the tips of the corrugations until pressed on the liners. Thixotropic effects were pronounced. Proportions recommended were 5 to 12 per cent of china clay and 24 to 38 per cent of sodium silicate solids. In the complete adhesive the total solids were 35 to 45 per cent, and the best  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio was 3.0 to 3.4/1.0. Treatment at 115 to 162° was also recommended after mixing the china clay and sodium silicate and water, and a steam pressure of 10 to 100 psi<sup>27</sup>. This gave a high degree of stability to the adhesive. A minimum amount of clay settled out upon standing.

Adhesive formulations for gluing together plaster board have also been prepared from combinations of sodium silicate and finely divided aluminum oxide<sup>28</sup>. Lander recommended the addition of a foaming agent such as ammonium laurate, triethanolamine, or various sulfonates to sodium silicate adhesives to produce a friable, porous mass instead of a solid<sup>35</sup>.

### Inorganic Cements in the Chemical Industry

Many of the major high temperature- and chemical-resistant adhesives employed in the manufacture of chemical processing equipments are prepared from sodium silicate adhesives and other inorganic binding agents. A few of the more significant ones are described below, though further types will be enumerated further on in a chapter on the application of adhesives to the ceramics field. Typical advertisements feature the resistance of sodium silicate adhesives to most concentrations of acids and alkalies—with the exception of hydrofluoric acid<sup>29</sup>.

Moore outlined in some detail a number of joining cements suitable for connecting links in chemical plants<sup>30</sup>. Among characteristics considered were: 1) chemical properties of the fluid, 2) temperature of materials, 3) ease of replacement, 4) durability of cement, and 5) permeability of the adhesive. Typical compositions which he listed were as follows:

Composition		Maximum Temperature (°C.)	Suited for
	(parts by weight)		
Sand	11	500	Acids
Powdered quartz	17		
Sodium silicate	7		
Litharge and glycerine		100	Ammonia
Powdered glass	10	500	Fixing glass or stoneware
Feldspar	10		
Kaolin	20		
Asbestos powder and sodium silicate	10		
Manganese dioxide	10	120	Alkali
Iron filings	40		
Portland cement and water	20-40		
Red iron oxide	5	180	Acids
Boiled linseed oil	1		
Barium sulphate	3	150	Acids
Asbestos	1		
Sodium silicate	2		

To be noted particularly in the above table is the mention of litharge and glycerine—long recognized as a permanent, strong adhesive employed in plumbing fixtures and the like. "Sauereisen" cements for ceramics, chemical plants, and electrical insulation are well known and widely employed by many industries. Stager reviewed litharge-glycerine cements, pointing out the dependence on the water content<sup>31</sup>. The best combination for pouring was recommended as formed from 4 to 5 parts of lead oxide to 1 part of glycerol, setting in two days. The set time may be hastened by adding an alkali<sup>32</sup>.

Another inorganic cement of note used in repairing castings and concrete consists of "Smooth-on" Iron cement<sup>33</sup>:

Precipitated iron powder	60 parts
Ammonium chloride	2 "
Sulfur	1 "

Water is stirred into the above mixture to form a paste which is pressed into cracks until sealed. Good adhesive qualities are exhibited. Another good cement for ceramics (including dentistry) and metalware is magnesium oxychloride. Care must be exercised, however, to have all proportions accurately measured and mixed. A typical combination is formed from 25 grams of calcined powdered magnesite, mixed to a smooth paste with a magnesium chloride solution of 24° Baumé. Braude lists a few typical inorganic cements as follows<sup>34</sup>:

Cement for Ceramics:	
Lithopone	10 parts
Powdered quartz <i>mixed with</i>	
Sodium silicate <i>to thick dough</i>	10 "
Iron cement for High Temperature:	
Powdered borax	1 "
Zinc oxide	5 "
Pyrosulite <i>in</i>	
Sodium silicate <i>to stiff dough</i>	10 "
Cement for Marble and Alabaster:	
Whiting <i>mixed and stirred with</i>	100 "
Zinc carbonate <i>in</i>	100 "
Sodium silicate solution	50 "

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## Chapter 14

### Theories of Adhesive Action

Technical advances in adhesives during the past several years have closely paralleled material developments in the plastics and rubber field. The usefulness of various plastics and modified rubbers as adhesives has not always been apparent from an examination of their chemical structure, though generally through empirical trials by plasticization or correct molecular weight distribution, adhesive qualities are developed. While tackiness or stickiness is accepted as a criterion for adhesive merit, modern synthetic adhesives are utilized in such a manner that this property of stickiness or tackiness is deemed of less significance than the permanency and physical qualities of the cemented assembly. The fact that animal and vegetable base adhesives may exhibit a tacky nature immediately upon application, of course, has little or no bearing upon the strength or permanency of the assembly effected. Adhesives which retain this tackiness may show an increase in the rate of creep under stress as compared with those having little or no tackiness. Many of the modern adhesives show no tackiness in their applied form, though under conditions of cure they establish excellent assemblies.

There are many factors which will influence adhesive action; these may be broadly grouped as physical and chemical. In both instances, the phenomena involved are closely related to the surface chemistry of the materials being bonded, and in examining the factors which determine adhesive action, reference will be made to current theories which will help us to understand these phenomena. Among the physical factors are: (1) Surface tension of adhesive. (2) Porosity of the surfaces being bonded, and their smoothness. (3) Physical properties of adhesive film (tensile strength, shear strength, compressive strength, modulus of elasticity, and creep rate). (4) Relative thickness of the adhesive film and its viscosity. (5) Method of applying the adhesive.

The last factor, the method of applying the adhesive, may in turn be analyzed according to the state the adhesive assumes at the time of application; physical changes in the adhesive occurring during the transition from time of application to its final, stable form; and pressures developed during the bonding. In fact, the method of applying and setting the adhesive

may be just as important as any of the other factors, inasmuch as an outstanding adhesive which may fulfill the ideal theoretical requirements is valueless unless applied correctly.

Chemical influences upon adhesive action are many, and although they have not been explored as intensively as physical factors, it has become apparent that the following are related to adhesion: (1) Polarity of the surface being bonded and the adhesive material. (2) Processes of polymerization, formation of by-products, and influence of molecular weight. (3) Nature of side groupings on polymer chain. (4) Thin films of gases or vapors adsorbed on the surface of the solids being bonded, and adsorption by adhesive films. (5) Evaporation or diffusion of volatiles from adhesive films. (6) pH of the glue line.

The processes of polymerization may, in turn, include a number of corollary factors related to molecular weight distribution, nature and frequency of cross-linking, and methods of effecting the polymerization. There is much basic information still necessary to explain many unusual phenomena which arise in establishing an adhesive bond. Small amounts of certain impurities may, for example, exercise important influences upon the bond. However, in the general over-all picture the selection and adaptation of an adhesive depend upon the chemical and physical nature of the surfaces being bonded. Although there are some versatile types of adhesives which are generally applicable to the majority of surfaces, an adhesive having outstanding properties for all surfaces and bonding problems is unknown. It appears therefore, that the development of ideal adhesives is closely related to the surfaces of the materials being bonded, and that each type of surface will have its own acceptable group of adhesives.

### Physical Factors Influencing Adhesion

**Surface Tension.** The suitability of a liquid adhesive for a given surface is related in part to the wettability of that liquid for the surface. The wettability, in turn, is dependent upon various factors including the viscosity of the liquid adhesive and its surface tension. The tendency of a liquid to spread or wet the surface of a material, is measured by the wetting angle, which is the angle of contact formed between the liquid and the surface. As the adhesion of the liquid for the surface increases, the angle of contact diminishes until a point is reached where the work of adhesion of liquid to solid equals the cohesion of the liquid, and the angle of contact vanishes.

To understand the contact angle, it is necessary to examine the surface tension of the liquids. Adam offers a clear description of surface tension<sup>1</sup>. In the interior of a liquid mass, the molecules are surrounded on all sides

and are subject to attraction in all directions, whereas at the surfaces there is no comparable outward attraction to balance the inward pull. Hence every surface molecule is subject to a strong inward attraction, perpendicular to the surface. This causes a diminution in surface area, and when the inward pull is large, the droplet tends to form a spherical shape.

Work must be done against the inward attraction to bring molecules to the surface. Work must be done in extending the surface. A hypothetical tension acting parallel to the surface is equal to the free surface energy (caused by inward pull of molecules). The mathematical equivalent of this free surface energy is the surface tension of the liquid. Among the factors related mathematically are viscosity, wetting angle, and surface

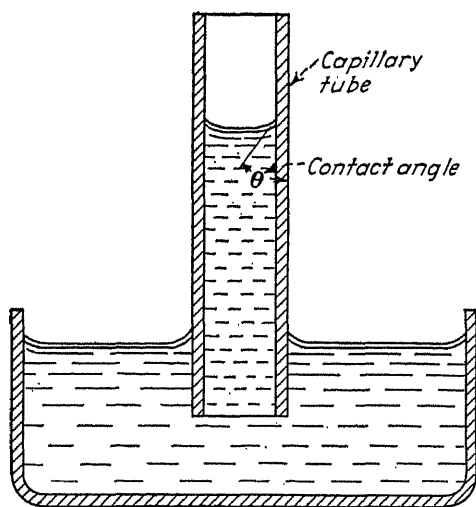


Figure 42.  
Rise of liquid in capillary tubes.

tension<sup>2</sup>. Surface tension is measured by a rise of liquid in a capillary tube as follows:

$$\sigma = \frac{h \times d \times g \times r}{2 \cos \theta}$$

where  $h$  = height of rise in capillary tube

$r$  = radius of capillary tube

$\sigma$  = surface tension, dynes per centimeter

$g$  = acceleration due to gravity

$\theta$  = contact angle (see Figure 42)

$d$  = density of liquid

When a tube is immersed in a liquid, the liquid wets the tube and rises until the surface tension pulling the liquid upwards is counterbalanced by

the force of gravity pulling it downward. The equilibrium point is denoted by  $h$  in the above equation. Typical values for the surface tension of liquids at 25° are shown in the following table<sup>2</sup>:

Material	Surface Tension (dynes/cm)
Water	71.8
Carbon tetrachloride	26.1
Benzene	22.3
Aniline	43.2
Ethyl Alcohol	21.8

It must be remembered that the above liquids, with the exception of aniline, are frequently employed in formulating adhesives. It should further be noted that the surface tension of all liquids decreases as the temperature is raised, and at the critical temperature, where the liquid becomes indistinguishable from a gas, the surface tension becomes negligible. For many liquids the rate of change of surface tension with temperature is a constant—equal to  $2.2^3$ :

$$\frac{d\sigma}{dT} = -K$$

The use of heat in curing the adhesive and causing it to flow before setting, may be assumed to contribute to lessening its surface tension. In studying the application of liquids to solids and the attraction of the solid for this liquid there are many considerations including: surface tension of the liquid, and its vapor; surface tension of the solid; interfacial tension between solid and liquid; concepts of hydrogen bonding; and polar characteristics. The application of the liquid to the solid generally results in a lowering of the free surface energy of the solid through equilibrium with the saturated vapor of the liquid. The work of adhesion (work required to separate the two) between the solid and the liquid has been shown by Harkins and Livingston to depend upon the surface tension of the liquid and this lowering of free surface energy of the solid<sup>4</sup>. Freundlich has also pointed out that the attraction of the solid for the liquid (adhesion tension) is equal to the difference between the surface tension of the solid and its interfacial tension against the liquid<sup>5</sup>. In other words, the attraction is greatest when the interfacial tension (contractile force operating at right angles to plane of interface and equal to difference in surface tensions between solid and liquid and its vapor) is smallest.

The Bartell cell is a useful device for measuring the attraction of a solid for liquids. The adhesion tension is measured in a displacement cell, into which the finely powdered solid substance is introduced. A liquid with poor wetting qualities is displaced by a liquid with good wetting qualities

and by calculations based upon flow through minute capillary pores in the solid substance the adhesion tension for various substances is noted<sup>6</sup>. Harkins and coworkers investigated a method of measuring the heat of wetting when a solid is immersed in a liquid<sup>7</sup>. The heat liberated is directly related to the energy of attraction between the two substances. He applied these measurements to the selection of vehicles for pigment particles in paint and varnish manufacture.

In considering the processes of adhesion it should be recognized that the typical adhesive is seldom a pure substance and the solid body rarely free of an adsorbed film. For solutions, Gibbs was the first to deduce the mathematical relationship between surface concentration and surface tension<sup>8</sup>. This may be expressed in the following manner:

$$\frac{d\sigma}{dc} = -\frac{\mu RT}{c}$$

where  $\sigma$  = surface tension

$R$  = gas constant ( $8.313 \times 10^7$  ergs/C°/mole)

$C$  = concentration

$T$  = absolute temperature

$\mu$  = gram moles of solute per sq cm of surface

Whenever two components are present in a liquid whose surface tension is lowered by the addition of the solute, it is evident from the above equation that the surface concentration of this addition product is greater than in the bulk of the solution. Thus a small addition to a liquid may cause a large effect in decreasing surface tension.

It may also be reasoned from this equation that if in the preparation of an adhesive material there is a distribution of high molecular and low molecular weight components, the low molecular weight fractions will concentrate on the surface more so than in the body of the liquid. From the standpoint of some adhesives, this is a desirable condition, because of the greater chemical activity and penetrability of the lower molecular weight fractions.

Solid surfaces are generally contaminated with foreign matter—a thin grease-like film, an adsorbed film of gas, or an oxide film. The greasy films may be substantially removed by appropriate chemical washings, but the adsorbed gas film is retained with great tenacity. In the practical application of adhesives, the presence of the adsorbed gas film might as well be assumed. Harkins and Bangham have determined the decrease of the free surface energy of a solid through the adsorption of a vapor upon the surface. The reduction of the free surface energy of the solid, and hence of its surface tension, may be deduced from Gibbs' adsorption equation<sup>9, 10</sup>. Presumably then, the adhesion can be increased between a solid and liquid

adhesive, if the adsorbed gas film is removed. The oxidation of aluminum and aluminum alloys by chemical or electrolytic means to reduce adhesion, has for example been studied<sup>11</sup>. Cleanliness of surface is generally recognized as a decided asset to good adhesion.

Schofield and Rideal have pointed out that as the length of the hydrocarbon chains in soluble fatty acids increases, the lateral adhesion between molecules in the gaseous film at the surface increases, until there is enough lateral adhesion to form a coherent film<sup>12</sup>.

**Porosity of Surface and Relative Smoothness.** The porosity of the surface and its relative smoothness will influence the behavior of adhesives applied to this surface. Materials such as wood, ceramics, paper, or leather are porous in the sense that numerous capillaries are present which will conduct away the more highly mobile portions of the adhesive, disturbing the balance of the solute and solvents or molecular weight distribution of the polymers. This is often an advantageous occurrence, as for example in the application of the sodium silicate adhesives, where the removal of water by diffusion through the capillaries of the porous surface results in rapid development of tack and quick-drying properties. In other examples, such as in plywood manufacture, too rapid a disappearance of the mobile portions of the adhesive may leave a "starved" glue joint.

We are indebted to Smekal for a graphic description of the surface of crystalline materials such as metals<sup>13</sup>. He describes crystalline surfaces as consisting of a mosaic of small blocks, with a number of minute cracks, fissures, or grain boundaries of small dimensions. Zwicky estimates the blocks of a definite average size of  $10^{-4}$  to 100 Angstroms, separated from each other by fissures<sup>14</sup>. Estimating the specific surface area is difficult.

The surfaces of organic high polymers, amorphous in character, present a different picture submicroscopically, with certain chemical groups predominating—depending of course upon the conditions under which the surface is formed. If the surface is formed on the evaporation of solvents, it is probable that those chemical groups which show the greatest affinity for the solvents, will be rotated towards the disappearing solvents. On the other hand, forming the surface under heat and pressure may cause minor proportions of other materials to concentrate on the surface, in accordance with Gibbs' equations. Other alternatives possible in solid organic plastics are created by processes of mechanical orientation—as though stretching, unidirectional flow, or calendering operations. These processes will orient the long chain high polymers, at least in the surface regions. The movement of liquids or vapors through organic high polymers are essentially dependent upon the chemistry of the particular material and are discussed further in this chapter.

Rideal<sup>2</sup> (p. 175) discusses various methods of determining the specific

area of solids, though the accuracy of these may be open to some question. Among the methods suggested are: comparison of a known smooth area against an unknown mass by solution rate; rate of evaporation from a surface or attack by a gas; and electrical resistance measurements on the surface of electrical bodies. The last method may be effective for metals, when the examination is conducted at high radio frequency.

Considerable importance has been attached to the specific surface area of materials being bonded by those authorities claiming that adhesion is largely caused by mechanical solidification about microscopic protruding fibers. McBain and Hopkins in their early investigations on adhesives reported: "It may be safely concluded that adhesion is a mechanical solidification of gel around and upon minute fibers"<sup>15</sup>. Considerable exception to this finding appeared in later investigations<sup>16</sup>, though in the final report it was contended that the adhesion of glue to wood was largely mechanical and only slightly specific<sup>17</sup>.

In a more recent survey of adhesives and adhesive action Rinker and Kline compared the work of McBain and associates with that of Browne and Truax<sup>18</sup>. Evidence of the latter group pointed largely to specific adhesive effects in bonding wood. Microscopic examination revealed that in drying, the glues deposited upon the cell walls of the wood, contracting from the center. In other experiments, though the pores were filled by wood stains, when the surfaces were lightly cleaned by fine sandpaper, good adhesive joints could be prepared.

It is a well known fact that some sanded wood surfaces will not bond as satisfactorily as the planed natural wood grain, because the former may be filled with coarse dust which will hinder good bonding properties. It is also common practice in the woodworking industry to roughen slightly hardwood surfaces to improve the bond. However it may be demonstrated that when properly planed and level wood surfaces are bonded together to form the thinnest glue joints, they give the highest strength values. This has been the generally recommended practice<sup>19</sup>. If the surface is deeply scored, bubbles may be entrapped in the glue line. Such points of interfacial discontinuity will be detrimental to the strength of the bond.

With respect to the cementing of wood surfaces, it is generally recognized that a penetrating adhesive does not contribute much to the strength of the glue joint. On the contrary, the adhesive tending to remain at the glue line may give the best results.

The adherence of precision-finished steel gage blocks is the subject of much theoretical discussion, and an experimental observation favoring polar attraction. While gage blocks have never been finished to the accuracy or smoothness of molecular dimensions, they have been made to an

accuracy of  $10^{-6}$  inch. After rubbing the blocks together it is very difficult to separate them by a normal pull perpendicular to the surface<sup>20</sup>. The importance of thin surface films in promoting adhesion between the gage blocks has been pointed out<sup>21</sup>. When perfectly clean the blocks fall apart by their own weight. Typical results with thin surface films are as follows:

Film	Normal Force to Pull Gage Blocks Apart (psi)
Lubricating oil	30
Turpentine	41
Condensed water vapor	50
Condensed water vapor and trace of soap	125

Bickermann conducted an examination of the adhesion between metal surfaces with different thicknesses of paraffin wax joints. Thin joints were observed to be stronger than thick ones—the difference attributed to the higher probability of a weak spot in the thicker specimen<sup>22</sup>. However, when true gap-filling adhesives are employed in which no volatiles or appreciable fillers are present to contribute to porosity of the glue line, the adhesive strength developed should be independent of the glue line thickness, provided an adhesive film is used which has strength properties comparable to the material being bonded. On the other hand, adhesives formulated with a considerable proportion of volatiles may be expected to yield high strengths only with very thin glue lines<sup>23</sup>.

Glass beads have also been the subject of adhesion experiments. They have been observed, for example, to adhere well when a thin moisture vapor film is present on the surface. On the other hand they do not adhere at all when perfectly dry and clean, or when they have been completely immersed in water<sup>24</sup>. Although the solids will show a strong normal adhesion to one another, it must be recognized that true welding occurs only at a few high spots, with the surface film filling up the gaps in elevation where the solids are in real contact. A perpendicular removal will interrupt the molecular attractions, while in sliding the bridges are sheared and new ones formed.

**Physical Properties of Adhesive Film.** The physical properties of the adhesive film influence to a large measure the character of the cemented assembly. While an evaluation of the physical properties of the cemented assembly is always significant, the properties of the film itself are not to be overlooked. McBain and Hopkins examined the physical properties of adhesive films in tests on a number of glues and reported: "It is suggested that direct tests of film strength are more unambiguous than any other single test of a glue."<sup>25</sup> To this well expressed thought should be added

another recommendation to the effect that in determining the physical properties of the adhesive films, tests should be performed upon those thicknesses which will be employed in service. In this manner the poor physical properties of non-gap-filling adhesives can be detected. Wherever possible, drying of the test film should be performed under conditions comparable to those of the intended application, as drying upon an open plate or pan is conducive to homogeneity and the best properties. McBain observed film tensile strengths as high as 12,000 psi in tests on high grade animal glues<sup>25</sup>. In this same series, torsion and shear tests upon gelatin glues, gum arabic, nitrocellulose, litharge-glycerine, canadian balsam, shellac, shellac-creosote, fish glue, rubber, and isinglass were reported. Shellac-creosote combinations used between non-porous, smooth metal surfaces showed exceptional results as high as 2500 psi in tension and shear.

The dependence of mechanical properties of adhesives upon humidity and rate of loading has also been determined for some adhesives<sup>26</sup>. The tensile strength of typical adhesives at 55 per cent relative humidity and room temperature are as follows:

Isinglass	13,000 psi tough
High grade gelatin	12,000 "
Nitrocellulose	8,500 " ductile
Starch	7,000 " ductile
Silicate soda	500 " brittle

The strength of these adhesive films far transcends the strength of the ordinary glue joint, largely because of differences in drying or curing, and the homogeneity of the glue line film. The effects of humidity can be readily determined, however, and the probable behavior of the cemented assembly under moisture extremes predicted. For example animal glue adhesives which are quite high at 0 per cent relative humidity, have practically zero strength at 100 per cent relative humidity. In this respect the synthetic resin adhesives behave much more satisfactorily at moisture extremes than adhesives from animal or vegetable sources.

One of the most important physical properties of adhesive films is the modulus of elasticity, which reflects the ability of the glue to absorb and distribute the loads from one surface to another. It may be pointed out that from a structural viewpoint, a modulus at the glue line comparable to that of the materials being bonded would be most desirable. This is however, difficult when bonding metals with organic plastics, because of the wide differences in the moduli of the two materials.

In structural applications where adhesives may be under sustained loadings, creep under stress may seriously affect the efficacy of the glue joint.

The more highly plasticized material is apt to creep under stress more readily than the stiffer, more rigid thermosetting material. In tests on glued metal joints, the long-time stressing of thermoplastic adhesives reduced the apparent strength of the assembly<sup>22</sup>. This is readily understandable, if it is recognized that during the process of stressing, shear or tensile loads are rupturing the adhesive bonds originally established after application. A true, permanent adhesive bond possesses negligible creep under the stress of the intended application. This property must be examined more fully than it has in the past, if true adhesion is to be realized, rather than a temporary sticking effect.

Additional problems are introduced when the adhesive layer and the materials being bonded have very different thermal coefficients of expansion. Under temperature variations, considerable physical stress may be introduced at the glue line. It has been shown, however, that the addition of finely divided inorganic powdered materials, such as aluminum oxide, to the adhesive will reduce its expansion coefficient to a range more comparable to glass and metals<sup>23</sup>.

More recent investigations of plastic masses employed as adhesives reveal a definite relationship between their physical properties and surface adhesive forces<sup>29</sup>. However this does not mean that the greater the tensile strength of a film, the greater will be the adhesive strength. In fact, there is a limited range in which the optimum adhesive properties can be obtained. This arises from the fact that adhesive films must also serve as load transmitting mediums, and must possess within themselves adequate cohesive strength if they are to function as an acceptable adhesive. Consequently adhesives are formulated in such a manner that a proper balance is maintained between good specific adhesion for the intended surfaces and good cohesive strength within the material. For thermoplastics this is accomplished by the selection of appropriate plasticizers, on the addition of which cohesive strength decreases and adhesive strength increases. For thermosetting polymers this may be accomplished to some extent by plasticizers, though more usually by proper molecular weight distribution at the time of application. Lower molecular weight fractions, it was pointed out earlier in this chapter, will move towards the surface and secure chemical bonding, while the higher molecular weight fraction within the adhesive will establish the necessary strength and rigidity.

The retention of volatiles at the glue line contributes in no small measure to the weakening of the adhesive film and the loss of its cohesive strength. The removal of these volatiles depends largely upon how the glue is applied and the condition of the surfaces being bonded. The non-porous types will, of course, retain the volatiles more readily, and short open

assemblies during which the volatiles do not evaporate too fast, will also result in lower strength films at the glue line. The too rapid evaporation of the volatile may cause the formation of a sealing surface film, retarding the passage of other volatiles before an assembly can be made.

The method of stressing the adhesive film may also influence the apparent adhesion in another manner. The true adhesion may be considered as measurable by a force applied normally to the surface, while tangential reactions to the surface (as for example when the adhesive film is stressed in shear) may in fact take into account frictional considerations. If the resistance due to friction is an appreciable quantity of the whole, then the shearing force,  $P$ , will bear a pronounced relationship to the normal load applied against the glue line.

$$\text{Total Apparent Adhesion} = fL + P$$

where  $P$  = either the load required to rupture the adhesive film attachment to the surface or the load required to cause failure in the adhesive film (whichever is smaller)

$f$  = coefficient of friction

$L$  = normal load

It is a well known fact that when failures in the material appear (as for example 100 per cent wood failure in testing blocks of wood), we have not evaluated the true shear strength of the glue. The shear strength test value is the most commonly employed factor for evaluating the strength of an adhesive. Likewise, it must also be admitted that when failure occurs in the adhesive film, we have not evaluated the strength of adhesion of a glue for a particular surface, but rather the tension or shear strength or combination of both of the adhesive film. Films with good cohesive strength will reflect this quality by high tension, shear, torsion, or compression strength. The films should be prepared according to the intended methods of application. Very detailed studies of static friction have been carried out by Hardy and his collaborators<sup>30</sup>. Kline and Rinker reviewed the elastic and plastic deformation phenomena of high polymers in relation to their employment as adhesives<sup>18</sup>.

**Thickness of Adhesive Film and Viscosity of Adhesive Solution.** The physical properties of the adhesive film are related to the thickness of the adhesive film which is formed, and the percentage of voids due to the evaporation of solvents. While the true adhesion of the adhesive film for the surface of the solid is independent of the thickness, the solvent employed may have some bearing due to the particular polarization induced at the interface upon its evaporation.

The viscosity of the adhesive solution is related indirectly to the film

thickness in that for a given solids content, the more viscous solution tends to form the thickest film with the most voids. Hence, the greater the probability of loss in cohesive strength of the adhesive film, when employing highly viscous adhesives. When the pressure of assembly exercises sufficient control of glue line thickness, this factor is of less consequence. Generally, the thinnest films prepared from solvent type adhesives, exhibit the greatest bond strength in assembly.

Corollary to these suggestions is the fact that if adhesive films are formed from 100 per cent liquid adhesive products containing no volatile matter, the apparent strength of the assembly will be *independent of the glue line*

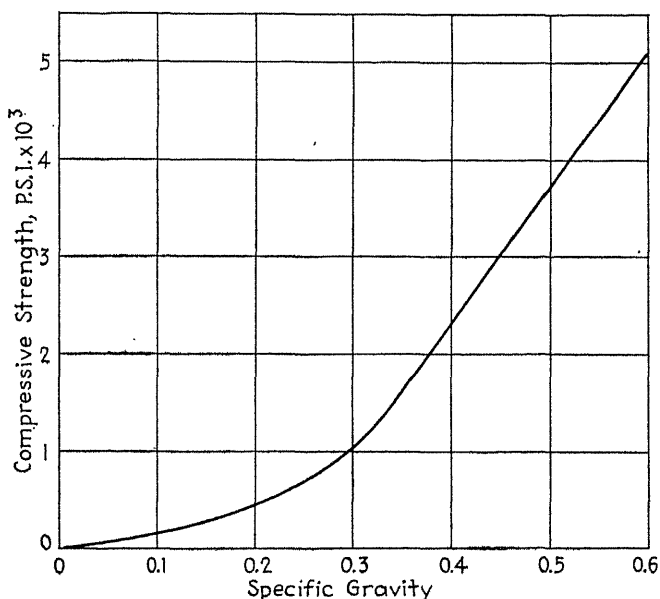


Figure 43. Characteristics of phenol-CH<sub>2</sub>O foams of different densities.

(Engel and Trozell)

*thickness.* The writer has performed numerous tests purporting to evaluate apparent shear strength as a function of glue line thickness, and has definitely established the previous premise for 100 per cent liquid furane adhesives<sup>49</sup>. On the other hand, solvent type adhesives show a very marked drop in strength with increase in film thickness. The fall-off in strength is caused largely by the absence of full homogeneity in the glue line due to the presence of voids, and the probable lower specific gravity of the substance of the adhesive film. Other data which should prove of fundamental importance to the relationships between film thickness of adhesives containing volatiles and the apparent strength are shown in Figure 43. These tests performed upon foams of varying density estab-

lish the relationship between properties of a given high polymer and its specific gravity<sup>31</sup>. They were taken from a paper by Engel and Troxell, and demonstrate the properties of an expanded phenol formaldehyde resin at different densities. Also significant is the fact that the properties of these expanded foams depend much on pore size.

The higher the viscosity of an adhesive the more readily it appears to adhere to vertical surfaces or moving surfaces—though for most adhesives viscosity is substantially a transient phenomenon dependent upon numerous chemical influences. It will be recalled that small additions of high polymers, such as polyisobutylene, to lubricating oils greatly increase the adhesion of the oils and greases for rotating metal parts, as well as the viscosity of the oil. Similarly small additions of high polymers to organic solvents or plasticizers greatly increase their viscosity and presumably their instantaneous adhesion to various surfaces. This adhesive effect is permanent only if the high polymer, which may be assumed to be the non-volatile portion, possesses the necessary chemical adhesion; otherwise the adhesive qualities are entirely a function of the properties of the solution. In all probability, creep under stress and poor chemical resistance characterize the adhesive containing polymer, solvent or much plasticizer. In the development of thermoplastic adhesives, various adhesive and cohesive agents have been the subject of many patents. These agents, generally established through trial and error, effect an optimum combination of cohesive strength of the film and adhesive strength for a given surface. The relationship between cohesive strength and intrinsic viscosity as a function of plasticizer content may be expected to follow from the data on creep. The viscosity of adhesives does influence the rotational characteristics of polar groups of high polymers, and because of this fact a high polymer may owe its good specific adhesion characteristics to the lower viscosity imparted to it by a solvent or a plasticizer. For cold- or room-temperature-setting adhesives prepared from high polymers, a viscosity low enough to insure adequate polar adjustments is necessary. On the other hand, high-temperature-setting adhesives may not acquire their mobility until placed under heat and pressure.

The temperature-viscosity characteristics of these polymers are most important. Heat welding is a satisfactory and effective manner of completing an assembly between mutually compatible polymers. Evidence points to the fact that temperatures promote a softening at the surface. It may also be concluded that chemical compatibility is a necessity because dissimilar thermoplastics, *i.e.* ethylcellulose and polymethyl methacrylate, will not successfully heat weld to one another, though they will to themselves. Chemical compatibility may be measured in terms of mutual polar relationships.

Difficulties may be encountered in heat welding some grades of polymers because either the temperatures for heat welding are too high, and products of decomposition may form too rapidly, or plasticizer separation may result in the abnormal concentration at the interfaces of the materials to be bonded. Not only do the processes of heat welding produce a pronounced lowering of viscosity or softening at the surfaces of the high polymers, but the temperatures involved are generally high enough to evaporate organic impurities and cleanse the surface to some degree. Among those impurities may be thin films of moisture, which interfere with good bonding of water-repellent types of materials. There is much in favor of heat welding as compared to solvent welding; not only can stronger assemblies be completed, but with care a union can be effected, as in the case of high polymers, which is invisible to the eye, except when examined under polarized light.

The viscosity-time characteristics of the thermosetting polymers are of a peculiarly advantageous nature in adaptation to adhesive problems. The lower viscosity of the partially polymerized masses permits favorable polar adjustments at the interface of the adhesive film and then as the mass polymerizes and the viscosity increases, cohesive strength is developed. Another premise to recognize is that maximum adhesion is not necessarily exhibited by the lowest molecular weight portions or at the time of lowest viscosity. However, the surface to be bonded has the favorable advantage of being exposed to a wide variety of molecular weights and at an appropriate time the optimum polar arrangements will be formed. Subsequent failures will probably occur in the film adhesive until the film has been fully cured, due to lack of sufficient cohesive strength. When fully cured, however, the film exhibits its maximum cohesive strength, and further failures may occur either in the film or at the interface owing to a true adhesive failure between the bonding material and the surface. In the case of laminated phenolics, up to 3000 psi the failures are all within the adhesive film because of the absence of sufficient cohesive strength. As the film continues to cure in this particular example, it acquires a strength beyond that of the material being bonded (laminated phenolic canvas base). Failures above the range of 3000 to 3500 psi are almost entirely in the phenolic material being bonded<sup>60</sup>. Three stages of shear failure are in evidence:

*Stage I*—Failure in the glue film due to insufficient cohesive strength.

*Stage II*—A transition stage in which failure occurs at the interface—partly in the glue and partly as evidenced by pockmarks or separated fibers on the face of the material being bonded.

*Stage III*—Complete failure in the material being bonded—an ideal condition from the adhesive viewpoint.

**Methods of Application of Adhesives.** The methods of application of an adhesive material influence the strength of adhesion indirectly. The method is, of course, dependent partly upon the physical form of the adhesive—that is, whether it is a prepared film, liquid, powder, or combination of these. Liquid adhesives lend themselves to brush, spray roller-coating, or dipping for application to the intended surfaces.

Pressure, temperature, and time, are three variables which have a bearing upon the ultimate strength. Temperature and time will influence the adhesive strength only in the sense that they determine when a film has been completely cured or dried. On the other hand, pressure may have a bearing upon the ultimate adhesive strength because it directly determines the amount and thickness of the adhesive film. There can be no general law which indicates the pressure to apply to surfaces being bonded, inasmuch as this pressure depends upon the flatness of the surfaces; the extent to which the liquid glue may disturb the dimensional stability of the material to be bonded; the relative fluidity of the glue at the temperature of application and cure; and the mechanical equipment available for developing pressure. Theoretically, zero pressure will suffice in bonding materials if the surfaces being joined are perfectly flat. There is no better example of this than carefully fabricated pieces of thermoplastics which are fitted together and joined by one or two drops of solvent cement applied at the interface of the two surfaces. In fact, for non-porous surfaces particularly, excessive pressure may cause the glue to squeeze out at the sides, leaving a starved glue line and poor adhesion. This has been a particularly aggravating problem in the bonding of metal surfaces which will tend to squeeze out most of the adhesive unless the adhesive has previously been dried to remove all volatiles and partially set-up, if of a thermosetting nature.

For porous surfaces, pressure appears desirable until the adhesive has developed sufficient cohesive strength to keep the assembly together. As will be indicated in the chapter on wood adhesives, it has been found that for certain glues and for certain types of wood there are optimum bonding pressures. Among other variables in the methods of application which may effect the final bond strength, are considerations of the time lapse between the application of the glue and the time parts are assembled. The loss of volatiles, the absorption of oxygen from the atmosphere, and miscellaneous chemical changes occasioned by spreading the adhesive into a thin film will be examined in subsequent pages.

### **Chemical Factors Influencing Adhesion**

**Polar Characteristics.** That the polar characteristics of an adhesive influence the strength of adhesion is generally accepted, although the im-

portance of this basic characteristic has been the subject of much debate during the past 15 years. For example, in the bonding of wood veneers some authorities (McBain, Lee, etc.) placed emphasis upon mechanical adhesion rather than true specific adhesion which others in this country (Forest Products Laboratory) upheld. There is a large mass of data accumulating which should throw more light on the subject. From a practical viewpoint much of this data has appeared for relatively pure compounds and the influence of impurities or binary mixtures may alter the situation. For organic compounds the covalent or homopolar bond predominates, rather than the electrostatic forces of attraction of inorganics. However electrostatic attraction applies not only to ions but also to dipoles and induced dipoles, and hence influences organic adhesives.

It has generally been considered that substances with but feeble polar groups possess small adhesion since polar groups are strongly adsorbed. DeBruyne pointed out quite emphatically that strong joints can never be made to polar surfaces with non-polar adhesives or vice versa<sup>32</sup>. This question has been examined for wood bonding, asphaltic binders, and for many adhesive films. Let us review briefly some of the dipole moments of different materials. Molecules with permanent electric moments are called polar molecules or dipole molecules. The phenolics, urea resins, and cellulose derivatives are formed of polar molecules, while on the other hand, polystyrene and polyethylene are non-polar. In the following table are listed dipole moments for a few important atom groupings<sup>33,34</sup>. These moments are generally determined in dipole-free solvents and extrapolated to infinite dilution. One dipole moment unit equal to  $10^{-18}$  e.s.u. is termed one Debye.

Dipole Moments for a few Atom Groupings

Bond	Moment (Debye Units)	Bond	Moment (DebyeUnits)
C—H	0.4	O—H (Phenol)	1.56
C—Cl	1.54	O—H (Water)	1.58
O—CH <sub>3</sub>	1.23	N—H(NH <sub>3</sub> )	1.66
NH <sub>2</sub>	1.54	C=O	2.8
Benzene	0	NO <sub>2</sub>	3.9
Hexane	0	C≡N	3.94

When two dipoles are aligned head-on the energy of attraction  $E$ , is given by the formula:

$$E = \frac{2U_1U_2}{Dr^3}$$

$U_1$  and  $U_2$  = dipole moments

$D$  = dielectric constant

$r$  = distance separating them

This force of attraction may be used to explain the affinity of various compounds and liquids for one another. Induced dipole attraction may also be possible for non-polar materials, when it is remembered that while the net moment of the molecule is zero, there are positive and negative parts which may induce mutual attraction.

The special structure of the molecules may be deduced from the specific angles formed for different linkages. The rotation of certain groupings about the molecule may be assumed to be in such a manner as to promote improved adhesion between adhesive films and surfaces to be bonded. This rotation is more readily possible in an adhesive which is mobile by virtue of its liquid consistency or temperature.

Adams discusses a number of the properties of the molecule which are learned from studying surface films<sup>1</sup> (p. 92). These properties depend in a large measure upon the polar characteristics of the molecules. They may be summed up in the following manner:

(1) Molecules of long chain compounds are elongated, much longer than wide, depending upon the molecular weight. They are flexible, however, and rotations can take place. In a series of tests upon the dipole moments of long chain polymers with dipoles at either end, Bridgman established the fact that the dipole moment for these molecules was in accordance with their molecular weight<sup>35</sup>.

(2) The molecules orient themselves quite steeply to the surface, depending upon the polar attractions at the interface. Those groups compatible with water (OH, COOH, NH<sub>2</sub>, etc.) align themselves towards the water phase, promoting strong attachment.

(3) End groups are different in size and shape from the groupings in the balance of the molecule. These are of importance to the physical arrangement of the molecules. However, when the chain lengths are long, the side groupings are the most significant members in determining the chemical behavior.

There is much evidence to support the influence of polar groupings on true adhesion. Trillat observed that in the application of fatty acids to metal surfaces there was evidence that the carboxyl radicals faced towards the metal surface, while the hydrocarbon groupings permitted easy slippage of the hydrocarbons of the second molecular layer<sup>36</sup>. Riedel discussed the influence of polar groups on the adhesives of tar<sup>37</sup>. Grader pursued this same line of thought, adding 5 per cent or less of various organic compounds to bitumen. Mono- and dicarboxylic acids and esters were tested, and alcohols and phenols. He concluded that adhesive power was due too adsorption of polar groups, but independent of the chemical reactivity of these groups. Dibasic carboxylic acids were very effective<sup>38</sup>.

Tests upon gliding friction and interfacial tension revealed that friction

was a minimum with non-polar materials such as benzene, heptane, and cyclohexane, while with acids and alcohols there was greater friction with increasing molecular weight<sup>39</sup>. This point was also made by Rideal, who showed a relationship between adhesion and molecular weight of a series of alcohols<sup>3</sup>. The results are reproduced in the accompanying Figure 44. In the test, the adhesion was determined by the force required to separate a steel cylinder from a glass plate flooded with different lubricants.

Campbell reported improved adhesion to metal surfaces using polyvinyl chloride acetate containing 0.1 to 4 per cent of maleic acid<sup>40</sup>. The maleic acid did not react with the polymer, but nevertheless served to improve adhesiveness. Improved adhesive properties were imparted to polyvinyl acetate adhesive through alcoholysis of approximately 30 per cent of the

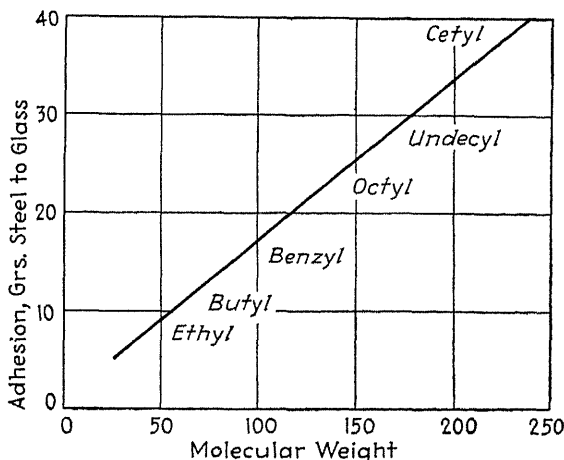


Figure 44. Relationship between adhesion and molecular weight of different alcohols. (Rideal)

ester groups. The reaction was carried out under anhydrous conditions in the presence of dry hydrogen chloride. The hydroxyl groups were derived from methyl alcohol<sup>41</sup>. Similarly the adhesive properties of acrylic acid esters were improved by subjecting the polymers to prolonged hydrolytic action to increase polar groups<sup>42</sup>.

Frictional behavior between mild steel surfaces lubricated with solutions of long chain organic compounds in oil was examined by Frewing<sup>43</sup>. Transition from smooth sliding to stick slips occur at a characteristic temperature for each solution. Adsorption of halides upon the steel surface is favored, owing to the interaction between the dipole of C—Cl and the surface. Each solution builds up and is in equilibrium with an adsorbed and oriented film of a polar compound on the surface.

Regarding the non-polar polymers, low bonding strengths are reported

in some instances except in the presence of certain addition agents, which may be plasticizers or fillers. For example, polyisobutylene sheets applied as tank linings have their adhesive strength improved almost 10 times through the addition of carbon black as a filler (2 parts of carbon black to 1 of polyisobutylene)<sup>44</sup>.

Not only the chemical groupings in the adhesive film, but also those on the surface of the material being bonded play an important rôle in the establishment of good adhesive bonds. In the bonding of metal surfaces, general practice suggests a thorough degreasing and cleaning before application of an adhesive coating. Adhesive shear strengths of the order of 3000 to 3500 psi have been obtained upon both steel and aluminum surfaces with the aid of organic plastic adhesive films, with occasional tests going higher in value. At the time of writing this has appeared to be the limit, though there is no reason why greater values will not be attained—at least to the limit of the shear strength of the adhesive films themselves, which for thermosetting compounds appears to be around 7000 to 8000 psi. In the chapter on the subject of metal bonding this point is pursued more fully.

Regarding pretreatment of steel surfaces, “bonderizing” and “parkerizing” with the aid of phosphoric acid solutions have not only tended to improve the corrosion resistance of the metals, but have also aided in the adherence of applied surface coatings. Presumably they should aid the adhesion problem. Some films will exhibit good adhesion to a surface when used alone as a coating agent. This same material may be less satisfactory when it is called upon to fill the gap in the cementing of two surfaces. In metal bonding it has become good practice to apply a primer coating to the metal surface, and to use another material for the actual cementing operation; the cement adheres to the first primer coat rather than to the metal surface.

As the outstanding adhesives are reviewed, the presence of strong polar groups appears to be the rule rather than the exception. For thermosetting materials, the following groups offer strong polar characteristics: (1) OH group in the phenolic resin series, (2) C=O and NH<sub>2</sub> groups among the amino resins, (3) OH group of furfuryl alcohol resins, and (4) carboxyl groups of the polyester resins.

When the resin cures *in situ* at the glue line, there is an opportunity for favorable polar adjustments to develop optimum qualities. Among the thermoplastics, the OH groups in the polyvinyl resin series appear most useful in realizing outstanding adhesive properties. Useful polar groups appear among the cellulose derivatives, particularly cellulose nitrate, though there may be some question about the degree of rotation of these high polymers which exist as micelle units, or families of long chain mole-

cules. The adhesive properties developed should reflect the nature of the plasticizer and solvent employed to aid in softening and polar adjustment. Chlorinated rubber derivatives have shown good bonding to metal surfaces. It will be remembered that the C—Cl polar bond is strongly adsorbed at clean metal surfaces.

Successful bonding of wood and cellulosic structures appears to be best accomplished when there is some moisture in the wood (8 to 12 per cent) and an adhesive material with polar groups possessing affinity for water and mutual attraction to the cellulosic hydroxyl groups. The partially cured thermosetting resins, proteins, and animal glues fulfill these requirements very satisfactorily. It has also been proposed that hydrogen bonding rather than polar characteristics accounts for the successful bonding to cellulose<sup>45</sup>. The present synthetic resins, starches, and proteins noted above are amply supplied with groups which can form hydrogen bonds to cellulose or water. Hydrogen bonding is ascribed to resonance between two structures, in which the hydrogen joins the atoms, producing inter-chain forces. At the same time molecular attractions are entirely possible through dipole-dipole, or dipole-induced dipole forces.

There are other methods of attraction between molecules which may involve the sharing of mutual electrons. This type of attraction leads to the complexities associated with the bonding of organic molecules. The presence of Van der Waals forces between molecules explains in part the forces of attraction between the acrylics or the polystyrenes, for example. These forces account for energy relationships between molecules rather than the electrostatic forces between single elements.

**Polymerization and Molecular Weight.** Somewhere between the more highly polymerized and the unpolymerized fractions lies a range of molecular weight or degree of polymerization best suited for adhesive purposes. We have ample evidence of these data among the thermoplastic polymers. In the process of cyclizing natural rubber, for example, a molecular degradation leads to an adhesive with much better properties. The best adhesives from polyisobutylene are not the toughest films with the highest molecular weight, but rather the semi-solid fractions. Polyvinyl esters show best adhesive properties in an intermediate range. Adhesives from cellulose derivatives are prepared from molecules which have undergone some degradation. The intermediate range of hardness among the coumarone-indenes appears best suited to adhesives. Among animal glues, the strongest types (grades 9–12) lie in an intermediate range of viscosities and jelly strength. The strongest starch adhesives are prepared by an acid pretreatment, followed by treatment with an alkali, the initial step giving greater solubility, and possibly some molecular breakdown to a more favorable range.

In analyzing this evidence, the solubility characteristics of the polymers must be kept in mind, inasmuch as they vary from one degree of polymerization to another, and it sometimes is the more favorable tolerance for solvent or plasticizer which explains an improved performance as an adhesive. Thermoplastic adhesives are polymerized before application, and therefore require more judicious selection of their molecular weight ranges than the thermosetting polymers; the latter are polymerized *in situ*, and expose a greater selection of polymers, the most favorable of which are adsorbed on the face of the material being bonded. The growth of a disorderly thermosetting structure has been used to explain the adhesive strength of phenolics during polymerization<sup>46</sup>.

Josefowitz and Mark recognized that sticky and tacky vinyl polymers were formed within the range of 50 to 300 degrees of polymerization<sup>47</sup>. The average length of the molecules should be considered inasmuch as the molecular weight fractions may vary from the lowest to the highest. Among those factors favoring increased tackiness are: (1) increase in temperature, (2) degradation of certain high polymers, (3) certain side chain groupings, and (4) solvents and plasticizers.

The factors which minimize stickiness as cited in the above reference are: (1) temperature decrease, (2) crystallization, and (3) cross-linking agents.

Recognizing that the highest degree of polymerization yields the toughest films with the best cohesive strength and that the lowest degree of polymerization yields compounds which are usually mobile liquids, the optimum range of adhesive properties for thermoplastic polymers will be found in that range where good specific adhesion to the surface can be established and where the film possesses sufficient cohesive strength to establish permanency in the assembly. It may also be reasoned and confirmed by practice that the longer the polymer, the less readily it will adjust itself in the presence of a solvent or plasticizer to a favorable position where the polar groupings can be adsorbed on the surface. It appears practical to prepare a combination of high molecular weight fractions to establish adhesion to the surface. Plasticizers alone will not accomplish this; this fact may be proved by applying various plasticizers to the surfaces to be bonded and observing the negative results. However, when the plasticizers are low polymers like the complicated natural resins used for softening certain high polymers, some improvements in adhesive properties are forthcoming. The molecular weight does not have to be very high before some tackiness is evident, as in the case of the adhesive semi-solids prepared from rosin and rosin esters or various metallic naphthenates; however, good cohesive properties must be present before these materials are successful as permanent adhesives.

In reviewing previous chapters on the derivation of adhesives from high polymers, the following degrees of polymerization (number of monomeric units) have been cited as satisfactory ranges for good adhesion :

	Degree of Polymerization
Polyvinyl acetate polymers	60-200
Polyvinyl chloride-acetate	100-150
Polyethyl acrylate	80-150
Polyisobutylene	50-150
Polyamides	50-100
Chlorinated rubber	125 cps viscosity grade
Cellulose nitrate	150-300

Not only is good adhesion exhibited within these ranges of degrees of polymerization, but also good cohesive strength. Properties of the films will be found to vary with the degree of polymerization. The ideal combination should be possible with an intermediate degree of polymerization for specific adhesion and components with high molecular weight for best cohesive strength. As seen earlier in this chapter, according to the relationship between surface concentration and surface tension, it was suggested that the lower molecular weight fractions concentrate at the interface where they do the most good.

**Side Groupings on Polymer Chain.** The nature of the side groupings on the high polymer chain is of the utmost significance in determining the merits of the polymer as an adhesive. We have already seen how the polarity of these groups influences the adhesive action through adsorption on the surfaces of the materials to be bonded. The chemical nature, the length and the complexity of the side groupings are other factors. In the chapter on cellulose derivative adhesives, the work of Malm and Hiatt was cited, in which they determined the adhesive effects of different cellulose esters with 3 to 18 carbon atoms in the fatty acid ester side chain. Optimum properties were exhibited with 6 to 14 carbon atoms, preference being shown for a capric acid ester of cellulose<sup>48</sup>. The relation between the softening point and substituent is shown in the accompanying Figure 45.

Comparisons of various polyvinyl esters of the same degree of polymerization would be most helpful in determining the relationships between the chemical nature of the side chains and the adhesive effect. Polyvinyl acetate has proved very useful as a general purpose adhesive, and to a more limited extent, polyvinyl butyrate. Work upon the polyvinyl acetals has shown that best properties are obtained through a balance of the acetate, hydroxyl, and acetate radicals. There is ample latitude for control in all of these polymers to develop a broad range of properties.

Among the polyvinyl acetals, polyvinyl butyral is widely employed for

adhesive purposes, especially for safety glass. It is significant that this acetal is generally selected rather than the one obtained from formalde-

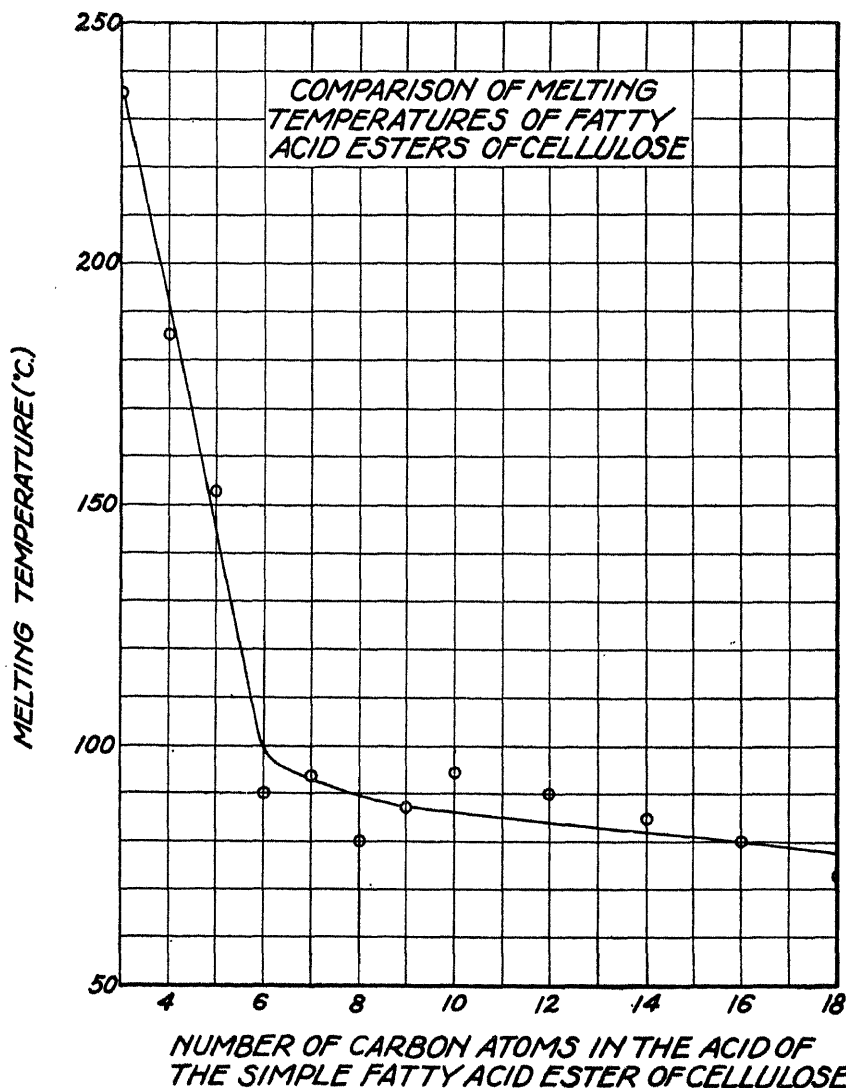


Figure 45. Relationship between melting point and side chain substituent for cellulose ester. (Malm and Hiatt)

hyde or acetaldehyde. Once again, the increased chain length of the side grouping appears to be of advantage.

In the chapter on acrylics, it was pointed out that progressively higher

homologues of the acrylic acid and methacrylic acid esters were successively softer, and apparently more useful for adhesive applications. It is noteworthy that polyethyl acrylate is considered a better adhesive than polymethyl methacrylate. For other adhesive formulations polybutyl methacrylate has shown promise.

Two factors appear to be directly related to the influence of side chains on adhesive action: polar characteristics and chemical compatibility. Polar characteristics have already been examined; chemical compatibility may be equally as important. The chlorinated vinyl polymers possess chlorine groupings which may exhibit strong adsorption on metal surfaces. However, the preparation of these materials into an adhesive or solution form for application is another problem complicated by the lack of solubility and chemical compatibility of these polymers. Consequently we do not find them employed very frequently as adhesives. The good compatibility of polyvinyl acetate with numerous solvents, plasticizers, and modifying resins, may be attributed to the acetate radicals attached to the chain.

If in the manufacture of the high polymer, cross-linking agents are introduced which will raise the softening point of the polymer, the chemical compatibility may be affected and the adhesive properties rendered less effective. However, if at the time of application of this adhesive, cross-linking agents are introduced which do not take effect until the polar groups have been properly adsorbed upon the surface, then the cross-linking may be of distinct benefit in creating improved cohesive strength. There is evidence of this, for example, in the employment of rubber adhesives, whereby vulcanization processes completed after the assembly and application of the adhesive result in the development of superior strength both in true surface adhesion and cohesive strength of the film.

The degree of substitution in cellulose esters or cellulose ethers has a bearing upon the adhesive properties of these polymers, largely because it determines the solubility characteristics of the polymers. There is a range—not at the degree of maximum substitution—where best compatibility with solvents is exhibited; from this range the selection of adhesive formulations can be made. The preferred range of degree of polymerization discussed earlier must not be overlooked.

The relative softening range of the polymer may be the criterion for the establishment of the adhesive formula. If hot-melt applications or heat welding are called for, it will generally be found that the intermediate degrees of substitution and long branched side chains will form the softest polymers; in fact some of these may be dissolved in plasticizers (without the use of solvents) at high temperatures to form useful adhesive materials.

Most of the discussion in this section has centered about thermoplastic

materials because the molecular weights of the thermosetting alkyd, phenolics, and urea resins are largely indeterminate. However, it is quite likely that side groupings influence adhesive properties as polymerization takes place *in situ*. While no experimental work has been conducted to prove this point, it is probable that higher aldehydes than formaldehyde, when reacted with phenolic constituents, will form improved adhesives. Acetaldehyde and acrylic aldehyde have given evidence of this.

**Thin Films Adsorbed on the Surface.** The influence of thin films of adsorbed gases or vapor upon adhesive properties bears careful examination. We have seen that metals are bonded most readily when clean, though probably not devoid of oxide films. When the oxide films are particularly thick, as in the case of electrolytic treatment, adhesive properties are observed to suffer. It remains for a systematic study to show relationships between gaseous films adsorbed on the surface of solids and the adhesive properties which can be developed. These studies would not dispel the necessity of coping with the practical exposure of surfaces to the atmosphere at the time of bonding; however, they may suggest new and better methods of achieving improved adhesive strength. Adsorbed carbon monoxide on metal surfaces may prove to be an asset.

The films adsorbed on the surface of solid high polymers may contain not only gases from the atmosphere but also gases absorbed from previous processing operations. More likely, however, the outside surfaces will reflect the gradual diffusion of volatile components.

If the adsorbed film is detrimental to adhesion, and the adhesive layer has a marked solvent action on this film, the problem of securing a good bond is solved to some extent.

The absorption of gases such as oxygen by the adhesive film after application to surfaces to be assembled, may be a very important factor in obtaining good adhesion, provided the oxygen contributes to cross-linking and the development of good adhesive strength. It is not always easy to determine whether or not the gaseous absorption is a major factor, because most adhesives show a change in properties upon evaporation of their volatiles during the open assembly period before the surfaces are finally pressed together. If oxygen is a factor in aiding the development of adhesion on the part of the adhesive film, air blowing the adhesive solution will prove beneficial. Rosin and hydrogenated rosin esters which will absorb considerable amounts of oxygen may, for example, prove to be more useful as a component of an adhesive formulation if that adhesive depends in part upon oxygen bridges. Drying oil components used in adhesives have also benefited from long open assembly periods, as these permit the absorption of gases which improve the properties of the final polymers. Certain thermosetting polymers also possess strong gas-absorbing tendencies.

**Evaporation and Diffusion of Volatiles from Adhesive Films.** The evaporation and diffusion of volatiles from adhesive films are important in the development of good adhesive strength. Except for the temporary benefits of permitting molecular rotation and polar adjustments, volatiles do not contribute much to the final adhesive properties. The removal of these volatiles may be classified as follows:

*From non-porous surfaces:*

- (1) Evaporation during the open assembly period
- (2) Slow diffusion to the edges after closed assembly
- (3) Polymerization of the volatile components

*From porous surfaces:*

- (1) All the factors of non-porous surfaces
- (2) Diffusion through the body of the material by capillary action or through channels of water already established.

If the development of the bond is to depend upon a film which is tacky because of the presence of a volatile (for example, in the cementing of paper and leather products), the same care must be exercised in the selection of volatile solvents for the adhesive as in the preparation of a surface coating. In large production, health hazards must be considered. Excessively fast evaporation rates are to be avoided to prevent skinning over of the adhesive film before the parts are pressed together. Likewise, rapid drying out of the adhesive from its container would be objectionable.

On the other hand if the presence of volatiles is detrimental to the final adhesive bond, the sooner the volatiles are evaporated the better. The tenacity of high polymers for organic solvents is remarkably high, and even though from weight measurements we may decide that the solvents have been substantially evaporated, "substantially" may still imply the retention of several per cent more volatiles. High temperature drying following low temperature drying will prove most effective. This may be observed, for example, in employing thermoplastic polyvinyl acetates in bonding metal surfaces. Appreciably better results are obtained when high temperature drying is practiced in addition to room temperature drying. In both instances heat welding should be employed.

The number of polymerizable solvents is very limited, yet there are some which may serve as useful vehicles for other polymers. Among these polymerizable solvents may be listed solvents such as mesityl oxide, allyl alcohol, furfuryl alcohol, furfuraldehyde, vinyl acetate monomer, methyl methacrylic monomer, and styrene monomer. Of course, the solvents are generally present in higher proportion than the polymers they dissolve and if a polymerizable solvent is employed, the characteristics of its polymer may overshadow those of original polymer.

In preceding chapters viscosity-concentration data are given for a

number of solutions of resins employed as adhesives. These may be referred to for further information. Where solvent cements are employed for thermoplastic materials, the rate of development of the strength is of course a direct function of the rate of evaporation and the rate of diffusion of the solvent through the material. This may be readily demonstrated in the employment of ketones of different vapor pressures as solvents for cellulose derivatives. The lower molecular weight ketones and those with highest vapor pressure will result in the strongest assembly within a given period of time.

Another factor which bears some relationship to the molecular weight is the rate of transmission through an organic polymer. This rate is also determined to a large measure by the chemical nature of the solvent, and may be determined from loss of strength as a function of time upon continuous immersion. Various solvent cements affect the strength of the thermoplastics they are bonding. The weakening effect of solvent cements upon thermoplastics and the tenacity with which these solvents are held are readily demonstrated. For this reason heat welding has its merits whenever the technique lends itself to the development of adhesive strength.

The presence of volatile solvents, including water, in thermosetting adhesive formulations presents additional problems. After polymerization has progressed to a certain degree, the solvents separate from the resin and establish mechanical voids if they are not eliminated. Their previous elimination is often impractical because polymerization may not take place until closed assembly has been effected. In addition, many of the reactions are of a condensation polymerization, liberating traces of water before final resinification.

For proteins, starches, and animal glues, water definitely has a plasticizing action and it is generally agreed that the strength and toughness of these films are attributable in part to the retention of water. Difficulties are encountered where there is a complete drying out of the adhesive film, leaving the structure embrittled. Cycles of low humidity followed by high humidity will reveal this weakness. In practice, assemblies will delaminate and fall apart.

Thin films of water on organic plastics or cellulosic surfaces have a marked influence on certain adhesives, particularly those which may be water repellent. Adhesive strength may be shown to be a function of the preconditioning accorded the sample of plastic being bonded. For higher humidities the adhesive strength falls off to very low values. For this reason thorough drying of the surfaces before bonding is to be recommended. Adhesives which will tolerate water are not affected to as marked a degree.

The wetting power of the volatile solvent and its penetrating character-

istic may alter considerably the strength of the adhesive bond. Strength is also a function of the molecular weight of the adhesive being applied. With better penetration, there is a tendency toward "starvation" of the glue line and consequently lower strength. Another deleterious effect to consider is the fact that a surface, such as wood or paper, is more likely to become embrittled, if it is easily penetrated by a resin. Embrittlement, as marked by a lower impact strength or lower shear strength, is wholly undesirable in the application of an adhesive. Therefore, to prevent excessive penetration, thermoplastic polymers in small percentages may be added to thermosetting formulations for the realization of higher strength. In assemblies where both penetration and bonding are desired, it is advisable to apply one resin for penetrating the structure, and another higher molecular weight material as the adhesive agent in a secondary operation.

**Acidity or Alkalinity of the Glue Line.** The influence of the pH of the glue line upon the adhesive strength has been the subject of much investigation. It is generally recognized that strong acids and strong alkalis are detrimental to the adhesive bond, particularly if they exert a pronounced effect upon the materials being bonded. Cellulosic bodies such as wood, paper, etc. are affected more than non-porous organic plastic solids or metallic bodies. Army-Navy specifications, such as ANG-8, state specifically that the pH shall not be less than 2.5. The problem appears usually for thermosetting resins, which depend upon a certain pH for their setting qualities. The neutral resorcinol-formaldehyde adhesives have an advantage over phenol-formaldehyde type, urea resins, and furane resins which depend on acid catalysts for their setting or polymerization. When these catalysts are not of a severe nature however, they are feasible for cellulosic structures and may give as good results as the resorcinol types. The fact has never been definitely established that less acidity means higher bonding strength. Of course, if the wood surfaces have been previously treated with alkalis, good bonding results are generally apparent—though it is open to question whether this is due to the pH at the interface or the lowering of surface tension and the better wettability of the adhesive. It must also be recognized that glue line pH may adversely affect the adhesive film rather than the surfaces being bonded.

It must be considered that the residual pH of many natural cellulosic structures is on the acid side to a slight extent, and an adhesive curing under the same acid conditions may be preferred. In bonding and pressing Masonite board, for example, a pH of about 4.1 gives optimum results. On the other hand, the bonding of organic plastics and vulcanized rubbers is definitely aided by a lower pH, as the acid-catalyzed adhesives appear to give excellent results for many of the polymers. Pretreatment

with acid or acid chlorides has helped subsequent bonding operations. For metals, acid cleaning and alkali rinses are only temporary in effect as the surfaces are substantially neutral. Free acids present may etch the surface, however, and improve bonding conditions, although free alkalis for materials such as aluminum may be detrimental. The combination of adhesive agents and aluminum type surfaces should not be made under conditions bringing about a Friedel-Crafts reaction, which might prove hazardous to the results.

Finally, it must be recognized that insofar as proteins and animal glues are concerned, their best spreadability depends upon their isoelectric points, though this fact is not often utilized in adhesive formulations. Many of the best water-resisting grades are dependent upon slaked lime formulations which keep the adhesives on the alkaline pH.

The problems of and factors influencing surface adhesions are many. Steps originally determined by trial and error are far more rational and take on new meaning when examined in the light of these factors. Too many surmises have been made in the past, however, and considerable room exists for more fundamental research.

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## Chapter 15

### Adhesives for Wood

The cementing of wood has long been a major concern of glue manufacturers, as probably more adhesives are sold for this purpose than for any other. Wood fabrication processes depend largely upon strong, durable adhesives, and every woodworking establishment has its own glue preparation facilities. Many animal and vegetable adhesives are applied to wood without the aid of heat, but with C-clamps and furniture clamps for assembly. Today synthetic resin adhesives augment the earlier types, with their advantages of water, mold, and weather resistance.

We are indebted to the Forest Products Laboratory for many valuable experiments on the durability of wood adhesives and for the development of improved types of adhesives. These findings have helped overcome problems in wood fabrication. Numerous bulletins reflecting the concentrated effort of many individuals have been issued by this organization on the subject of wood adhesives.

Any understanding of the correct application of adhesives to wood must be founded upon some knowledge of wood technology and the particular problems associated with different grades of wood. The data for bonding different species of wood under varied conditions before and after pressing are voluminous; and in making comparative tests, conditioning treatments should be equivalent. Consequently, when comparing the characteristics of competitive adhesives, a grade of strong wood is selected in order to stress the adhesive more severely. There are soft and hard woods; woods with and without pores; while heartwood reacts differently to adhesion as compared with sapwood. The influence of these wood variables on good adhesion is covered in this chapter. However, at all times we are dealing with a cellulosic structure with strongly polar hydroxyl groups attached to the cellulose chain. Keeping this in mind, as well as the necessity of controlled moisture in wood for favorable bonding, a broad selection of glues is possible. The water- and alcohol-soluble partially polymerized thermosetting compounds, starches, proteins, animal glues, etc., are a few of the many available. The actual choice of adhesive will be based upon the assembly to be completed and the manufacturing facilities available.

Some of the major fields of application of adhesives to wood fabrication processes are as follows:

- (1) Plywood manufacture and the production of flat panels.
- (2) Molded or curved plywood shapes, as for boats and aircraft.
- (3) Structural timbers and their lamination with adhesives.
- (4) Furniture and fixture construction with adhesives to effect the final assembly.
- (5) Resin impregnation and subsequent bonding.

Adhesives may be used for either of two main processes of wood fabrication: primary bonding operations and secondary bonding operations. In primary bonding the various layers of wood are joined into flat or curved structures with warm or hot setting adhesives, generally at the factory; while in secondary bonding cold setting adhesives effect assembly of wood elements to other structures either at the factory or in the field. For example, the bonding of reinforcing stringers or ribs to plywood skins is a secondary bonding operation, while the manufacture of plywood is a primary operation.

Two of the outstanding contributions of adhesives to wood fabrication processes are in the aircraft industry and building construction. To indicate the scope of such activities, the accompanying photographs speak for themselves. Figure 46 illustrates a wing section, measuring 320 feet in span, of the Hughes Aircraft Company's new giant cargo airplane. This is the largest airplane ever built—fabricated entirely from wood with the aid of wood adhesives. Hot setting phenolics were employed to bond the skin, and cold setting urea and resorcinol resins for the assembly and scarfing operations. Figure 47 shows a laminated arch, a construction featured in many buildings. Some very long laminated arches have been prepared (up to 125 feet), finding application in public buildings, auditoriums, churches, airplane hangers, etc. Glued laminated arches have been employed for many years in Europe.

The entire subject of adhesives for wood is so extensive that the work performed in this field overshadows the adhesive requirements of other industries. In this chapter emphasis will be placed upon the specific problems which adhesives are called upon to solve in wood fabrication, so that the designer or adhesives manufacturer can better cope with them. Perry has examined some of the problems of wood adhesives and fabrication, reviewing the field in an interesting and informative manner<sup>1</sup>. At the start of the second World War, useful manuals were prepared on the subject of wood aircraft fabrication and the design of wood aircraft structures<sup>2</sup>. These manuals summarized many bulletins of the Department of Agriculture, and reports of the Forest Products Laboratory issued up to that time. Stress analysis data for wood structures, included in the above mentioned bulletins, were particularly helpful because of the lack of organized material on the subject up to that time.

### Relationship of Wood to Its Gluing Characteristics

There are many wood variables which will influence the gluing characteristics. Several of these factors will be discussed in the following paragraphs.

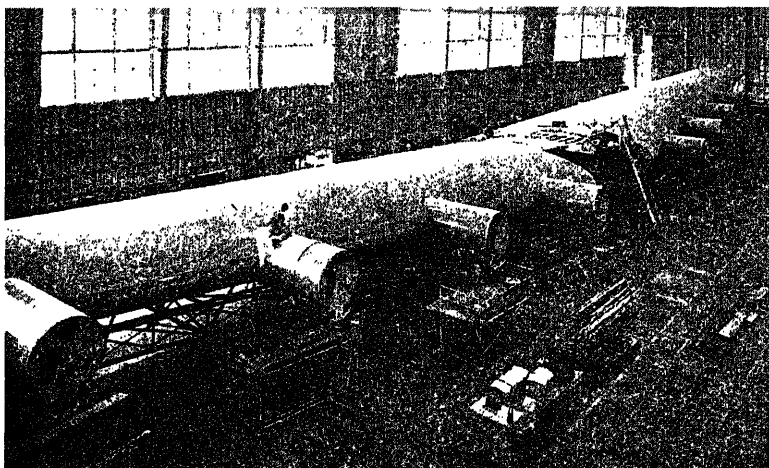


Figure 46. Resin bonded plywood wing section for large cargo airplane  
(Courtesy Hughes Aircraft Co.).

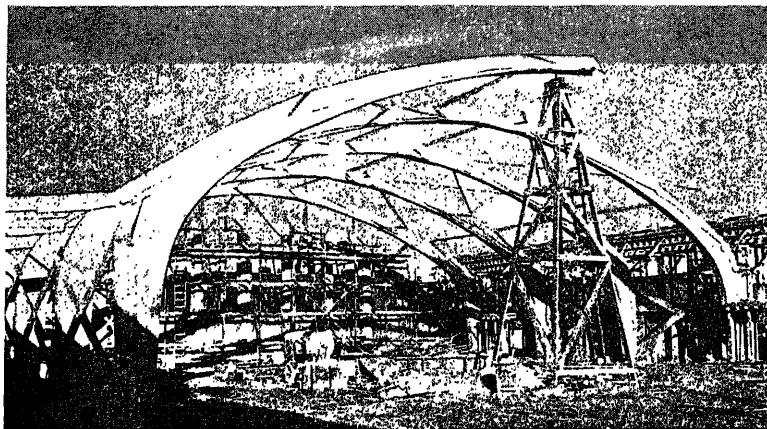


Figure 47. Structure of laminated arch construction (Courtesy Boeing Aircraft Co.).

**Type of Wood.** There are a large number of species of wood which require gluing. Bonding characteristics, while similar for a number of types, are nevertheless dependent upon the origin of the wood. From a gluing viewpoint the broadest classification of woods is on the basis of porous

(hardwoods) and non-porous (softwoods) varieties. In the former group are woods such as birch, maple, beech, ash, mahogany, oak, poplar, walnut, etc., while in the latter group are fir, spruce, hemlock, cedar, pine, etc. Truax has shown quite conclusively the relationship between the density of the wood, its shear strength and wood failure<sup>3</sup>, ranging from the lower density woods of cedar, pine, and fir to the higher density maple, hickory, and osage-orange. Hundreds of tests were performed upon about 40 species of wood, and results evaluated by block shear test (see Chapter 20). In this evaluation, animal, vegetable, and casein glues were employed. With the adhesives employed it was quite apparent that with higher density woods the percentage of wood failure decreases and the apparent shear strength increases. The non-porous woods are less subject to starved glue joints than the porous species of wood.

Markwardt and Wilson have presented a comprehensive and valuable analysis of the strength characteristics of various woods grown in the United States<sup>4</sup>. Complete physical data on various wood species are contained in their publication.

**Location of Wood in the Tree.** The portion of the tree from which the wood originated will influence its bonding characteristics. There are appreciable differences between heartwood and sapwood, the latter being more porous and containing fewer gums and resins than heartwood. Tests in bonding heartwood and sapwood show quite definitely that the percentage of wood failure and the shear strength are greater in the sapwood. The percentage of wood failure is taken as an empirical index of how well the assembly held. With 100 per cent wood failure, however, it reveals the weakness of the wood rather than the strength of the glue.

The way in which the wood was cut from the log influences bonding characteristics to an appreciable extent; first, because of the grain direction presented for bonding and secondly, because of differences in shrinkage and swelling characteristics. End grain to end grain assemblies are seldom made of wood, except perhaps in the application of balsa pieces to a stiff skin in a sandwich construction used on aircraft, where the skin carries most of the stress. Scarfing procedures which are generally employed are described later. Tangential and radial shrinkage of the wood are the most important shrinkage factors—averaging 7 to 9 per cent tangential and 3.5 to 5 per cent radial shrinkage for most species<sup>5</sup>. These values are for the green to oven-dry condition. The manufacture of plywood and laminated constructions must contend with differential shrinkage, which may overtax the strength of the bond.

Some veneers are rotary-cut and others vertically sliced, the latter generally being preferred for the strongest aircraft assemblies. There is a greater possibility of cross-grain in rotary-cut veneer, which influences to a

small degree the maximum strength obtained by gluing procedures. For furniture, however, figured veneers cut from burls, crotches, and similar growth irregularities are employed as face plies because of their decorative value. Relationships between the degree of cross-grain and the strength have been established. The porous woods most likely reflect decrease in bonding strength more rapidly with steeper cross-grain, as greater pore volume is exposed to the glue line.

**Moisture Content of Wood.** The moisture content of the wood at the time of gluing is an important factor. For most reliable results all components of wood fabrication assembly should be pre-conditioned to the same degree of moisture before assembly, as well as after assembly. The accompanying Figure 48, shows the relationship between the moisture content in wood and the prevailing humidity; the rapid moisture increase at

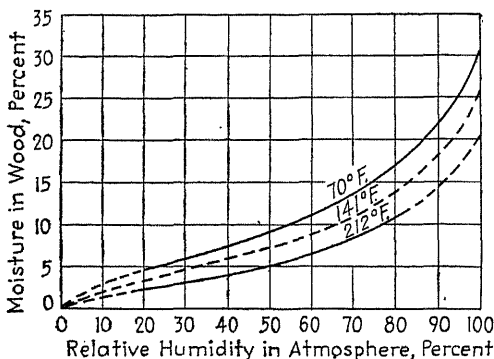


Figure 48. Moisture content in wood as function of relative humidity.

higher humidities is very apparent. Uneven moisture contents in wooden members will result in unequal swelling or shrinking, with subsequent warping and possible overstressing of the glue line. The most general range of moisture content recommended for wood bonding is 8 to 12 per cent.

Under changing atmospheric conditions, it is probable that glued wood structural elements tend to shrink or swell independently creating internal stresses at the glue line. This condition is even more pronounced when there are unequal moisture contents in the wood members at the time of assembly. Besides, the presence of water or water-soluble solvents will upset the uniform moisture balance at the time of assembly. In a series of tests upon hickory, spruce, and yellow birch, it was shown that important internal stresses which are not proportional to the dimensional changes occur in the joint when the moisture content is lowered below that of curing or assembly<sup>6</sup>. The effects are not as pronounced, however, when the mois-

ture content is raised higher than that of the gluing conditions. Moisture changes have a decided weakening effect on joints in which pieces are glued with the grain of the joint faces at right angles to each other, or when different species of wood are glued together. Strengths are determined by block-shear tests, although the paper points out that these tests are not necessarily related to larger laminated assemblies, where the effects are more pronounced. From an examination of glued timbers undergoing changes in moisture, it has appeared that delamination would tend to occur when the moisture content is being reduced<sup>6a</sup>.

It is logical to suppose that the higher the water content of the glue at the time of assembly, the greater will be the effect upon the moisture distribution in the wood. The protein resin adhesives have considerably more water and greater effect. Heavier glue spreads correspondingly affect the moisture balance of the wood to a greater degree. Cold gluing generally results in greater moisture introduction into the glue line, while hot pressing brings about a reduction in moisture content. The greater the distortion due to moisture gradients, the greater will be the pressure required at the time of gluing.

The effect of moisture content of veneers before gluing is shown in the accompanying chart of plywood prepared from three 1/16 inch birch veneers. The strength tests are made by the plywood strip shear test (see Chapter 20) for dry and wet conditioning. Wet conditioning is obtained by soaking the plywood test strips in water at room temperature for 48 hours before test. The phenolic resin employed in this test was in film form, substantially devoid of moisture, while the casein and urea resin illustrated were the cold setting type. It will be observed that the shear strength of the phenolic film is more critically dependent upon the moisture content of the veneer. Some moisture is necessary to aid in the proper flow during bonding, although higher amounts would reduce the specific adhesion of the phenolic for wood surfaces. Redfern and Fawthrop examined the effect of the amount of compression and influence of moisture content in producing exterior grade Douglas fir plywood<sup>7</sup>. A minimum specific pressure of 175 psi and a lower moisture content (less than 5%) was recommended than used in other practices. Low moisture content meant faster rate of heat transfer. Olson reported upon the effect of moisture content of wood in gluing birch and maple lumber as compared with thirteen room temperature setting and intermediate temperature setting phenol, resorcinol, and melamine glues<sup>8</sup>. Acceptable plywood joints were obtained with all phenolic glues, except a highly alkaline catalyzed one, at moisture contents of 2 to 25 per cent in the wood. The resorcinol glues likewise gave good results both for dry and wet strip shear and block shear tests for wood moisture contents of 2 to 25 per cent. On the other hand, the strength of

the melamine glued members fell off quite appreciably at low moisture content of 2 per cent in the wood. Their acceptable range was 6 to 21 per cent moisture content in the wood, though in practice, 8 to 12 per cent range is maintained.

**Preparation of the Wood Surface.** Quite important to successful gluing operations is the preparation of the wood surface for subsequent gluing. The wood should be machined to the proper surface for gluing only after it has been properly conditioned to the correct moisture content. Otherwise, further warping may distort surface preparatory measures. Smooth, uni-

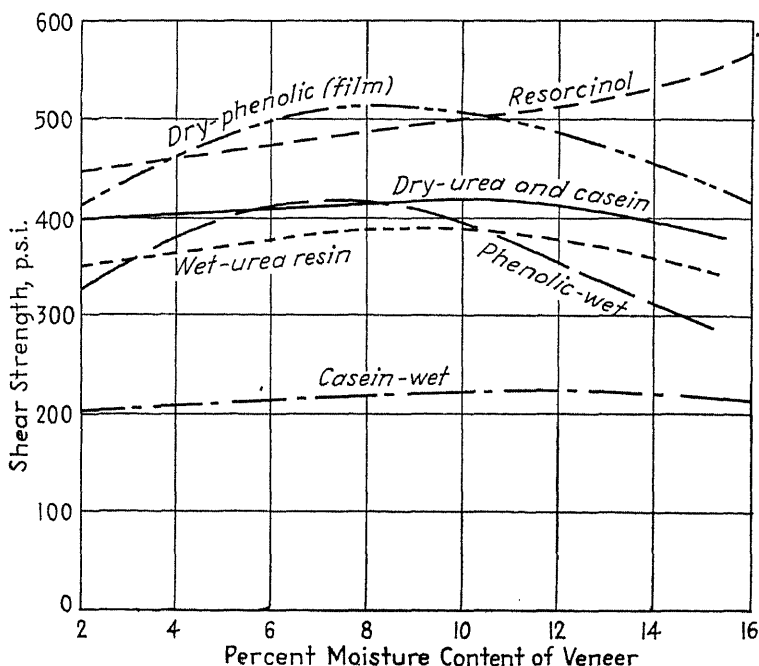


Figure 49. Effect of moisture content in birch veneer—on wet and dry strip shear tests.

form surfaces produced by planing or with jointers are best for gluing, and contrary to popular belief, rough, uneven sanding or smooth fine hand sanding may be objectionable. Machine finishing should be applied to the conditioned wood just before gluing to make certain of a true joint. Wood surfaces which have been excessively burnished in finishing may offer particular difficulty in gluing. Special machine sanders developed for finishing the surface of plywood, are also acceptable as they leave the surface well prepared for subsequent gluing. On the other hand, sawed surfaces are objectionable because they are not as true or uniform as planed surfaces and leave

torn fibers to which the glue tends to adhere with poor results. When surfaces are to be sawed, sharp, hollow ground blades which do not tear fibers should be used. Light hand sanding of plywood surfaces has been found very beneficial in correcting conditions interfering with adhesion of cold set glues. Danger of over-sanding is reduced by specifying 4-0 garnet for low density species and 3-0 garnet for high density species of wood. Reduction in face ply thickness should not exceed 10 per cent<sup>9</sup>.

In a series of tests designed to show the effects of various surface treatments on the bonding of wood, Maxwell prepared surfaces which were accurately planed, sanded, sawed, combed (furrowing wood surface with hack saw blade), and burnished (passing wood over a dull planer at slow speed)<sup>10</sup>. Cold set urea-formaldehyde resin adhesive was selected for test

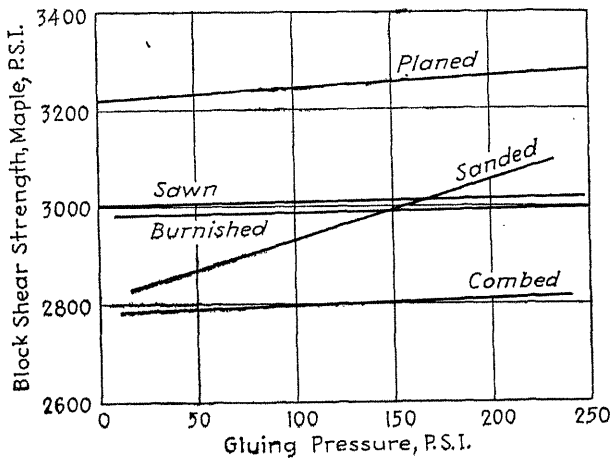


Figure 50. Effect of various surface pre-treatments— on shear strength of maple blocks bonded with cold setting urea resin adhesive.

and sugar maple blocks employed for the evaluation. The superiority of the planed surfaces is clearly demonstrated in Figure 50.

The processes of manufacturing plywood and treating wood veneers may cause added problems in bonding. De Bruyne discusses difficulties occasioned by case-hardened plywood<sup>11</sup>. Investigations at Royal Aircraft Establishment point to the mechanical damage on surfaces such as plywood, involving a loose surface layer which is easily pulled off. The development of resin impregnated wood veneers places the problems of bonding wood into the classification of bonding to organic plastics. Other types of adhesives are required for bonding to resin impregnated woods and papers. These are discussed in another chapter.

**Influence of Extractibles in Wood Surface.** The presence of chemicals

in the wood structure will influence the bonding characteristics. These may be extracted or their concentration altered by the solvent employed with the adhesive. That they have a decided influence on such properties as swelling and shrinking, has been pointed out by Stamm and Loughborough<sup>12</sup>, who classify them as water and organic solvent type extractibles. The presence or removal of these ingredients will affect bonding characteristics to some extent, by controlling the penetration of the resin adhesive. When materials such as crystalline urea, water-soluble phenolic or urea-formaldehyde resins are introduced into the cell wall of the wood, the subsequent bonding operations are rendered more difficult and the amount of penetration of the adhesive is less. On the other hand, where partial delignification of the wood veneers has removed some materials, improved penetration of impregnating resins or adhesives can be realized<sup>13</sup>.

In some species of wood, such as California redwood, the proportion of extractives is fairly large. The chief constituents are tannins and a water-and-ether insoluble material called phlobaphene<sup>14</sup>. The purified tannins contain 2.8 per cent of methoxy groups, 15.4 per cent of phenolics, and 20.3 per cent of hydroxyls, suggesting the presence of resin forming constituents. It is reasonable to expect that adhesives formulated to be compatible with and perhaps enter into chemical combination with extractives in the wood, would possess certain advantages over non-compatible types. However, the proportion extractable from wood veneers by the usual glue solvents is generally small and not deemed consequential.

**Bleed Through of Glue.** In the bonding of wood veneers, particularly wood with pores, bleeding through of the glue to the outside surfaces of the face plies may be somewhat objectionable. Adhesives which may acquire low viscosity under pressing conditions are prone to behave in this manner, and if of a dark color, may spoil the appearance of the face plies. The amount of bleed through is appreciably affected by moisture content of veneers at the time of hot pressing, slope of grain in the face plies, thickness and species of face veneers, amount of glue spread, and species and type of wood used for cores. If the amount of bleed through to a plywood surface is excessive, it may create an additional problem for secondary gluing operations to the plywood skin<sup>15</sup>.

### Nature of Adhesion in Wood

As brought out in the chapter on the theories of adhesion, there are numerous factors which influence true adhesion to wood surfaces. Wood is a strongly polar material, owing this property as well as its affinity for water to the presence of the free hydroxyl groups of the cellulose molecules. The polar type of water-soluble adhesive has appeared to be the best for wood products, but polarity alone is not the basis for determining good adhesion

in wood. Hydrogen bonding to the cellulose molecule is also considered a contributing factor. The fact that the smooth planed surfaces rather than the coarse sanded ones will develop the greatest strengths is indicative of the fact that mechanical adhesion is not the most important consideration.

The adhesive research committee of the Department of Scientific and Industrial Research in London devoted much attention to the nature of adhesion on wood surfaces. Their findings indicate that the adhesion is largely mechanical and slightly specific<sup>16</sup>. On the other hand Brouse and Browne report that the adhesion is largely specific, a viewpoint which has found wider acceptance in the industry<sup>17</sup>. Studies on the penetration of glue into wood have shown the theoretical benefit of roughened surfaces to be improbable<sup>18</sup>. McBain's experiments demonstrate that the staining of woods before gluing appreciably lowers the strength because presumably the pores are filled, preventing a good mechanical bond. On the other hand, Brouse and Browne repeated the experiments and lightly sanded the surfaces to clean them, without affecting the filled pores. Good joint strengths were obtained though penetration was greatly reduced as evidenced by photomicrographs. Phenolic rosin glue films have been examined after cure by treatment of the wood substance with *chromic* acid, and further data obtained for the study of specific and mechanical adhesion<sup>18a</sup>.

Recent efforts in blocking off the hydroxyl groups on the surface of wood veneers through vapor phase treatment with acetic anhydride, should prove useful in evaluating adhesives<sup>19</sup>. The importance of the hydroxyl groups in determining specific adhesion to wood surfaces could be determined upon cellulosic surfaces with various substituents at the hydroxyl position.

Water-soluble adhesives have long been deemed an asset in the bonding of materials for wood and cellulosic products. This is due not only to the affinity of the hydroxyl groups for water, but also to the ease of keeping equipment clean. However, this affinity for water is retained to some slight degree by the finished adhesive layer, as the final polymers comprise high and low molecular weight fractions.

### Conditions of Gluing Wood

Before we examine concrete examples relating to the application of adhesives to wood problems, it is desirable to explore a few more general aspects of conditions of gluing. Glues or adhesives for woods must fill very special requirements. In the first place, wood is a relatively porous material as compared to solid, organic plastics or metals, and because of this the adhesives are generally formulated differently. It has been pointed out that the porous woods will permit the adhesives to diffuse from the glue line into the wood, leaving a starved joint. This results not only in a decrease of

strength but also in some staining of wood veneers, which in plywood manufacture may be objectionable upon the outside face plies.

The following steps are taken in the application of adhesives to wood :

- (1) *Application of glue.* Hand brushing, spraying, or machine glue spreaders are employed.
- (2) *Open Assembly Time.* Before the glue coated surfaces are pressed together they may be exposed to the open atmosphere for a period of time to allow volatiles to evaporate.
- (3) *Closed Assembly Time.* The veneers or lumber coated with adhesives are stacked one above the other, so that there is minimum access to the atmosphere. Permissible closed assembly time is generally twice as long as open assembly time.
- (4) *Pressing and Curing.* The resin coated layers are pressed firmly together, with or without heat, depending upon the adhesive and the operation.
- (5) *Cooling and Removal from Press.* Some assemblies require cooling before they are removed from under pressure, while others can be removed while hot.

There are variations in the above procedure, depending of course upon the type of equipment available and the time cycles required. One of the most important phases is the open assembly period, because during this time the glue thickens either by processes of polymerization; loss of volatiles through evaporation or diffusion into the wood structure; or by the absorption of oxygen from the atmosphere. For porous woods, some thickening of the adhesive film is desired in order to minimize loss when pressure and perhaps heat are applied. The pressure will force the adhesive into the pores and capillaries into which it will penetrate at a rate depending upon its surface tension and viscosity. It may be undesirable to thicken the glue too much beforehand, because otherwise it may have a relatively limited life in the glue pot. Hence, the experienced wood fabricator knows the technique of thickening the glue on the glue line by proper control of open assembly time. The open assembly time depends upon the adhesive and the prevailing temperature. Lower temperatures will greatly extend the pot life and the open assembly time of synthetic resin adhesives. The viscosity of the more common wood adhesives varies from one type to another, though it is generally in the range of 100 to 3000 centipoises. It may be well to refer to earlier chapters dealing with viscosity of various adhesives versus the time in the pot after activation.

**Effect of pH.** Considerable discussion has taken place on the effect of glue line pH on the relative strength of the glue joint. An excessively strong acid or alkaline catalyst will either weaken the structure of the glue

or the wood fibers. The effect upon the wood physical properties has been determined by contacting wood veneer test specimens with glues of different pH values. Dowling's report on some of these tests is reproduced in the following table<sup>20</sup>:

Wood Veneer	Solution of Resin Glue	pH Resin-Catalyst Mixture	Ultimate Tensile Strength (psi)			
			1	2	3	4
$\frac{1}{8}$ " spruce	None	—	11,000	7,970	9,400	11,700
$\frac{1}{8}$ " spruce	Urea-formaldehyde	3.5	9,400	10,120	10,000	10,800
$\frac{1}{8}$ " spruce	Alkaline phenolic	8.5	12,200	9,400	10,500	10,000
$\frac{1}{8}$ " spruce	Acid-phenolic	1.54	9,800	7,780	10,400	10,000
$\frac{1}{16}$ " birch	None	—	11,000	7,340	12,000	13,300
$\frac{1}{16}$ " birch	Urea-formaldehyde	3.5	11,000	8,890	11,700	10,900
$\frac{1}{16}$ " birch	Alkaline phenolic	8.5	11,600	8,050	10,200	10,900
$\frac{1}{16}$ " birch	Acid-phenolic	1.4	9,700	7,130	8,600	9,700

*Test Conditions:*

1. Tested after curing and drying at 12% moisture content.
2. Roof exposure for 1 year.
3. 10 day cycle—24 hr. 100% R.H. at 100°F,—24 hr. at 165°F
4. 10 days' continuous heat at 165°F

For protein adhesives, a strong alkaline catalyst will deteriorate the adhesive in time, rendering it less effective. On the other hand, the urea resin types are affected by the strong acid catalysts, while the phenolics possess exceptional resistance to strong acids. In the case of the latter, the probable attack of the strong acid catalyst must not be discounted.

It has been noted that chemical treatment of wood surfaces improves the glue joints in certain types of wood<sup>21</sup>. Birch, maple, gum, oak, poplar, and walnut species were treated with a 10 per cent solution of sodium hydroxide; the excess was wiped off in a few moments. There was a marked improvement in strength values.

The pH of the glue is determined by its chemical nature and the conditions required to set it. In consequence, the pH is seldom adjusted to suit a particular wood, but rather the conditions generally have to be established to favor the curing requirements of the adhesive.

**Glue Spread.** The thickness of the glue spread upon wood is generally determined by the weight per square foot, or the weight per 1000 square feet. The latter value is more commonly employed to define the glue spread. Typical glue spreads are 50 to 60 pounds of urea-formaldehyde (wet, solids, approximately 60 per cent) resin per 1000 square feet or about 70 pounds (wet weight; solids, approximately 30 per cent) of casein glue per 1000 square feet. When long assembly periods are necessary, as for example in laying up laminations for a ship's keel, or when bonding porous

woods, heavier glue spreads are recommended. However, thicker glue lines do not always determine longer open assembly times because of the possibility of the film of adhesive skinning over and preventing a good bond of one surface to another. From a production point of view, however, it is important to ascertain maximum and minimum open assembly times for members to be bonded. The application of the glue and the press work is coordinated with this characteristic. Temperature and humidity controls are definite assets for obtaining uniform results. At all times a proper balance should be maintained between the consistency of the glue and the amount of pressure applied. The importance of maintaining uniform and sustained pressure has been brought out in a Forest Products Laboratory report<sup>22</sup>.

Perry suggests some typical wet glue spreads, which appear to be consistent with the average practice<sup>23</sup>:

Adhesive	Woods	
	Non-porous (lb./M sq. ft.)	Porous (lb./M sq. ft.)
<i>Cold Pressed</i>		
Synthetic Resin Adhesives	35-45	40-50
Other glues	70-85	80-95
<i>Hot Pressed</i>		
Synthetic Resin Adhesives	25-35	30-40

These values are given for the wet single glue line spread. If both surfaces are to be treated, the total amount should be increased some 25 to 50 per cent, though there is actually less per surface for a double glue line spread. The relative dryness of the wood, and the amount of cross-grain may necessitate the application of additional glue. In the accompanying chart the strip shear tests of birch plywood are evaluated as a function of the glue spread. The wet strip shear tests (see Figure 51), obtained after soaking for 48 hours in water, reveal the weakness of the low glue spread joints. Check the optimum properties against the values of glue spread suggested in the preceding table. From 8 to 12 per cent moisture content was present in the veneers employed in these tests performed at Forest Products Laboratory.

The amount of glue is controlled by weighing for small laboratory samples, and by adjustments on the glue spreading machine when veneers are passed through one right after another in production. For hand brushing of glue, as in building up of structural timbers, the experienced glue man can tell by appearance whether or not the glue spread is correct. Otherwise, it is a relatively simple matter to employ a wiping device which

will level off the glue to the desired thickness immediately after application and hence the necessary weight is automatically determined. For example, for a glue with a specific gravity of about 1.34, the initial glue spread should be about 6 mils thick for a weight of about 43 pounds per 1000 square feet.

**Glue Line Thickness.** It is a generally accepted fact that for solvent type adhesives, the thinnest joint produced is the strongest joint. While wood fabrication assemblies may strive for this condition through accurately planed surfaces, some irregularities may appear because of untoward moisture gradients or some warpage produced in the assembly which is not

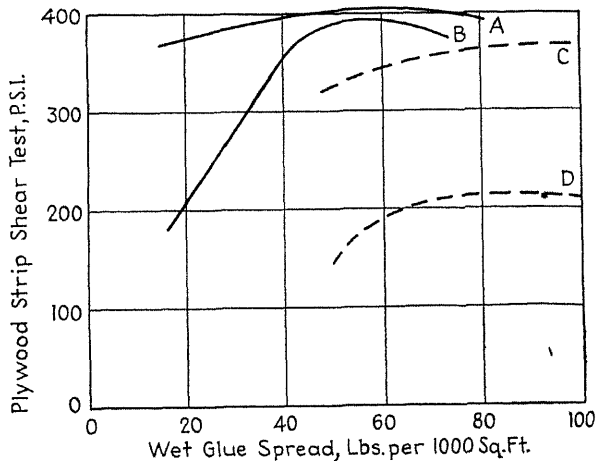


Figure 51. Influence of glue spread on strip shear strength type of adhesive.

- A—Cold set urea—dry strip shear test
- B—Cold set urea—wet strip shear test
- C—Casein—dry strip shear test
- D—Casein—wet strip shear test

recognized at the time of clamping. In any event a thick glue line may be present at some place in the assembly. For these and other practical reasons, it has been necessary to examine the effect of glue line thickness on the strength developed. The acid catalyzed phenolic and the acid catalyzed 100 per cent furane resin adhesives are unquestionably the best for developing thick glue lines. By various weathering and cycle tests, the discrepancies in other adhesives which have lower solids content may be brought out. The synthetic resin adhesives with high solids content have shown promise in developing true gap-filling adhesives.

It is imperative that glue manufacturers make available further data on the strength of their adhesives with different glue line thicknesses.

Nonvolatile adhesives appear best for the thickest glue lines. The simplest test possible is to pour or cast a section of the glue, measuring 1/16 to 1/8th inch thick. Examine this pouring after a week or so—it will soon tell whether or not crazing and cracking will occur in the adhesive when it is applied to assembly joints. Most commercial adhesives will crack and craze quite severely, almost precluding the possibility of determining physical characteristics on the film itself.

It is quite likely that the thicker the glue line, the sooner the specimen will fail under vibration fatigue tests, and while no comprehensive data have been reported as yet, this characteristic is one to be considered. In the practical assembly of large wood components in the field, there is a high probability that the glue lines at some positions may be excessively thick. Unless the adhesive is of a somewhat resilient nature, it will not exhibit good dampening qualities; it will fail early in vibration if it is of a porous, brittle nature.

An investigation of several adhesives for wood by Poletikan<sup>24</sup> reveals that joint strength is invariably proportional to the thickness of the glue line:

Glue Layer Thickness (Mils)	Number of Samples	Average Shear Strength (psi)	Average Wood Failure (%)
2	5	1500	37
3	5	1330	40
4	11	1450	25
6	6	1340	21
8	8	1100	19
10	9	1200	9
12	7	940	11
14	4	840	4
16	3	670	5
18	4	480	2
20	1	520	3

**Pressure Required for Gluing Wood.** The pressure is dependent upon a number of factors related to the physical makeup of the wood, which will not take excessively high pressures without permanent deformation. Most laminating of plywood takes place at pressures under 250 posoi. The amount of deformation in the wood under pressure depends also upon the presence of plasticizing agents, which may be water or synthetic resins. In the production of curved parts, always to be considered is the spring-back tendencies of wood, which may develop excessive stresses at the glue line. Moisture gradients may, we have seen, also contribute to internal stresses; slightly warped wood pieces may necessitate greater laminating pressures at the time of assembly.

Much of the assembly work involving wood components has been accomplished with various clamping devices including furniture clamps, C-clamps, jack screws and screw presses. The pressures derived from these may be quite high, measuring several thousands of pounds, though when properly distributed over a large area as through the use of caul blocks or their equivalent the unit pressures become quite low in values. Multi-opening hydraulic presses offer the greatest control in laminating pressure, but they are generally limited to flat press work. The merits of hot versus cold pressure will be discussed shortly in specific application to wood bonding problems.

The use of high pressures in bonding wood (over 1000 psi) has been particularly helpful in the manufacture of "Compreg," a phenolic resin impregnated wood structure. While the density of the final laminate is directly related to the laminating pressure, the physical properties have been moved up in accordance with this pressure, with a particularly great increase in the shear strength. However, the impact strength suffers, as the final impregnated laminate is not as good as a solid piece of wood in this characteristic. The manufacture of "Compreg" generally requires a separate adhesive at the glue line, as well as the original impregnating resin. Thin layers of phenolic resin film have served very well in this respect. Resin impregnated compressed wood is very much more stable in dimensions under moisture extremes than the untreated wood. The extent of the plasticizing effect of resin impregnation upon the compression properties of wood has been brought out by Stamm and Seborg<sup>25</sup>. Under hot pressing temperatures of 300 to 350°F, and 250 psi, spruce, cottonwood, or aspen can be compressed to one-half the original thickness while this treatment causes only a small compression upon dry wood. Under the same conditions gum and poplar require some 300 to 400 psi. Commercial grades of resin impregnated, compressed wood are generally prepared at pressures of 1000 psi or higher. Large flat press plywood is generally laminated at pressures of 150 to 250 psi.

The period of time pressure is applied depends upon the glue. Theoretically the time duration of pressure should be sufficient to enable the glue to develop strength to resist internal stresses tending to separate the glued members. It is obvious that cold setting adhesives must be under pressure for a considerably longer period of time than the hot press cycle, which may be completed in a relatively short period. In fact, the cold press plywood plants must devote a large portion of their floor space to accommodations for pressing and keeping stacks under clamps. For the long time application of pressure, as through mechanical clamping devices, there is generally sufficient creep in the wood to loosen the pressure of the clamp and cause a decrease in the amount of load that is applied, until

it is practically nil where thick sections are involved. Consequently the clamps must be tightened at frequent intervals if pressure is to be maintained. Hydraulic devices, presses, or dead weight loading maintain the necessary follow-up to keep uniform pressure. The time duration of pressure is a function of temperature as well as the adhesive, and in the following paragraphs the necessary data can be obtained from the charts for the various adhesives.

High pressures tend to force the glue into the wood structure, and if this leads to the formation of a starved joint, more glue should be spread at the glue line. High pressures can also be detrimental to wood veneers treated with large amounts of resin impregnant by causing the wood veneers to flow out and disintegrate. For styrene resin impregnated wood, this occurs at about 1000 to 1200 psi when large amounts of resin are present.

As far as general bonding requirements are concerned the following practical points are a guide to the bonding of wood:

(1) Sufficient pressure should be applied to bring all wood surfaces into intimate contact with one another.

(2) If hot pressing is applied the pressure should be kept on during cooling to avoid blistering or pronounced grain effects on face plies, or adequate breathing should be practiced to eliminate volatiles at the beginning of the cycle.

(3) Pressure should be distributed uniformly and maintained up to full requirements during the time the glue is setting. If the pressure is applied to only a few points, avoid localized compression failures by distributing the load through caul blocks. By spring loading and dead weights, the pressure can be determined; otherwise special dynamometers should be used for determining pressure.

(4) Assemble wood before pressing in as stress-free, stable condition as practical, properly treated to avoid warpage.

(5) Remember that as the glue is setting and being converted from a mobile fluid to a viscous mass, it is better to increase pressure slightly, rather than decrease pressure.

**Temperature Requirements in Gluing.** Most adhesives can be conveniently classified into hot setting and room temperature setting adhesives, with a few intermediate types classified as warm setting adhesives. The thermosetting synthetic resin adhesives are either converted by heat or catalysts, and if catalysts are active enough, room temperature setting proves practical. The catalysts may be in the nature of acids or alkalis or sometimes, certain resin forming constituents which have been withheld. For large productions, hot press gluing proves most practical, because the time under pressure is reduced and more square feet area can be turned out.

The adhesives for hot press work are not as soft or as mobile as those employed for room temperature cure, because the temperature generally causes the adhesive to acquire increased mobility.

The thermoplastics are generally classified as room temperature setting, except where the solvents are driven off before assembly, necessitating a hot press, heat-welded assembly which proves to be the most practical way of developing the best strength. Rubber base or synthetic rubber

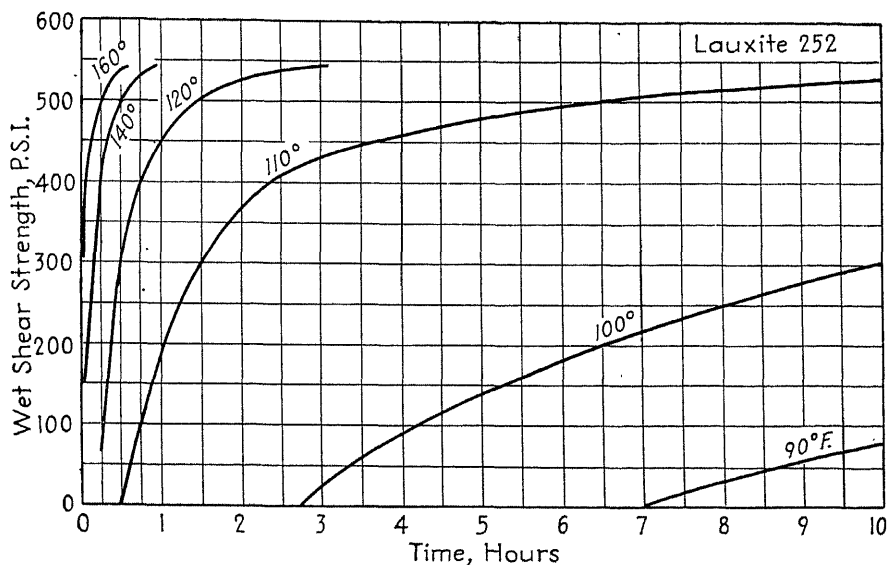


Figure 52. Wet joint strengths of 3-ply,  $\frac{3}{8}$ -inch yellow birch plywood glued with "Lauxite" 252, low-temperature melamine, for various lengths of time at several glue line temperatures. Specimens immersed in water soon after removal from the press and tested wet after soaking 48 hours at room temperature. (*Forest Products Laboratory*)

base compounds are generally vulcanized during application as an adhesive, and this may take place at room temperature or at elevated temperature.

On the other hand, animal, protein, starch base, or sodium silicate adhesives depend for their adhesive properties upon rapid changes in the water content of their formulations, brought about by diffusion into porous structures such as wood or paper. This characteristic is not as dependent upon temperature as in the case of the synthetic resin types, and in consequence these adhesives can be used at lower shop temperatures, whereas the synthetics may be at a disadvantage. The rate at which the adhesives gain in strength is the principal factor in determining the length of time parts are kept under pressure. Some exhaustive tests on the development

of joint strength in birch plywood have been reported for several low temperature setting synthetic resin adhesives for various periods of time<sup>36</sup>. Curing temperatures of 75 to 220°F were investigated, and the 1/16 inch birch veneers conditioned at 65 per cent R.H. and 80°F. In all gluing the temperatures were measured at the glue line with the aid of thermocouples. This is rather important, because of the time delay in attaining full curing temperature at the glue line. While this report was obtained upon yellow birch plywood, it was pointed out that resin glues do not cure at the same rate for all species of wood. Resorcinol glues cure at an

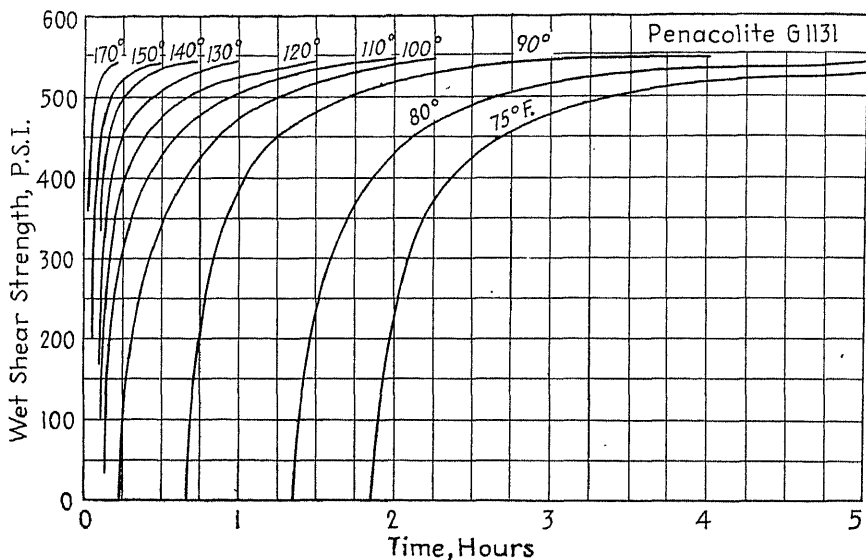


Figure 53. Wet joint strengths of 3-ply,  $\frac{1}{16}$ -inch yellow birch plywood glued with "Penacolite" G-1131, low-temperature resorcinol., for various lengths of time at several glue line temperatures. Specimens immersed in water soon after removal from the press and tested wet after soaking 48 hours at room temperature. (*Forest Products Laboratory*)

approximately similar rate on birch, spruce and mahogany, but more slowly on Douglas fir, white-oak and sweet-gum. The melamine glues cure at a similar rate upon birth and sweet-gum, but more rapidly upon fir, white oak, mahogany, and spruce. The phenolic resin glues appear to cure similarly upon birch, spruce, and mahogany, but more slowly upon fir, and still slower on white oak and sweet-gum.

Figures 52, 53, 54, taken directly from the Forest Products Laboratory report<sup>22</sup> compare a typical resorcinol-formaldehyde resin ("Penacolite G-1131"), melamine formaldehyde resin ("Lauxite 252"), and a phenol-formaldehyde resin ("Cacophen LT - 67"). These adhesives are all classified

as low temperature setting materials. The wet strengths were obtained by soaking the test specimens in water at room temperature for 48 hours. Where the strengths exceeded 500 psi it was difficult to compare one adhesive with another because the failures were almost entirely in the wood.

Having established a well-cured assembly, the next point to consider is the durability of this assembly, particularly at elevated temperatures. Continuous dry heat is deleterious to most glues. Among the synthetics, the ureas suffer the most sharply in this respect<sup>27</sup>. In sustained high

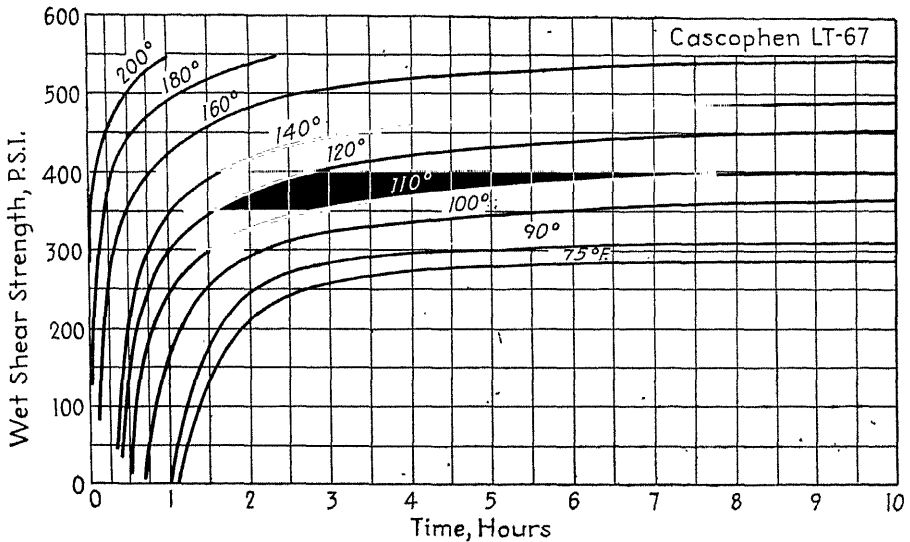


Figure 54. Wet joint strengths of 3-ply,  $\frac{3}{8}$ -inch yellow birch plywood glued with "Cascophen" LT-67, low-temperature phenolic, for various lengths of time at several glue line temperatures. Specimens immersed in water soon after removal from the press and tested wet after soaking 48 hours at room temperature. (*Forest Products Laboratory*)

temperatures of 200°F and 20 per cent R.H., the hot setting phenolics and the hot setting melamines held up best, though they lost about 30 per cent strength in four months. The changes were more pronounced among the low temperature setting glues. Casein glues proved better than ureas in resistance to high temperatures. Various other cyclic variations of temperature and humidity were applied to the materials under test.

In examining a typical time cycle for hot pressing, we are faced with the slow conductivity of the wood and the distance the heat must travel into the interior to cure the adhesive. In the plywood examples, which will

be given later in this chapter, the time is not long, depending upon the thickness and the moisture content of the veneers. On the other hand in the laminating of thick lumber, the time to introduce heat into the glue lines by thermal conduction is unnecessarily slow. Besides, the moisture balance may be upset and the effects of preconditioning altered. In consequence, special heat methods must be developed by ultra-high frequency heating, which will generate the temperature at the glue line<sup>28</sup>, or through special additives to the glues such as acetylene black, which will render the glue electrically conductive and susceptible to low frequency resistance heating<sup>29</sup>. An alternative method is the imbedding of wires into the glue line and heating the material by passing electrical current through the resistance wires<sup>30</sup>. A good summary of methods of heating

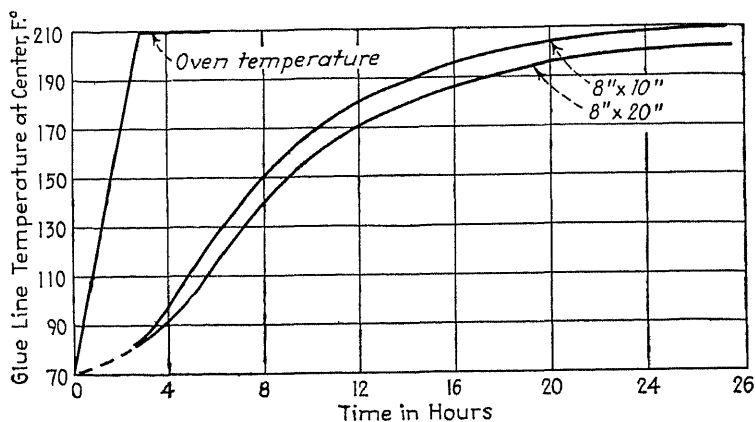


Figure 55. Lamination of white oak timber and rate of temperature rise.

the resin glues during assembly was prepared by the resin adhesives subcommittee of the S.P.I.<sup>31</sup>. These included the use of hot platens, ovens, resistance heating, infrared heating, and boiling water or steam baths. The latter method entails the immersion of a clamped assembly of wood veneers into a tank of boiling water during the curing period. It is well known that fluid mediums will more rapidly transfer heat than will air. It is significant also, that very little changes of moisture content were reported in the assemblies.

As a guide to the time required for heating thick laminations of white oak timber, the following curves are reproduced from a paper by Dosker and Knauss<sup>32</sup>. The laminations measured 8 inches wide by 10 inches high, and also 8 inches wide by 20 inches high. To avoid drying out of the timber, the humidity was kept sufficiently high to maintain 10 per cent moisture in the wood during heating. With the aid of low temperature setting phenolics, resorcinols, and melamine adhesives, it was possible to

develop good joints which demonstrated a high percentage of wood failure even after exposure to weather extremes and salt water. The problem of getting sufficient temperature to the glue line is difficult. In one assembly, the boiling water technique described in the preceding paragraph was employed, and the laminated timbers heated in a shorter period of time than in an oven<sup>33</sup>.

High frequency curing of glue lines in the assembly of wood components has proven to be an efficient means. There are advantages not only in

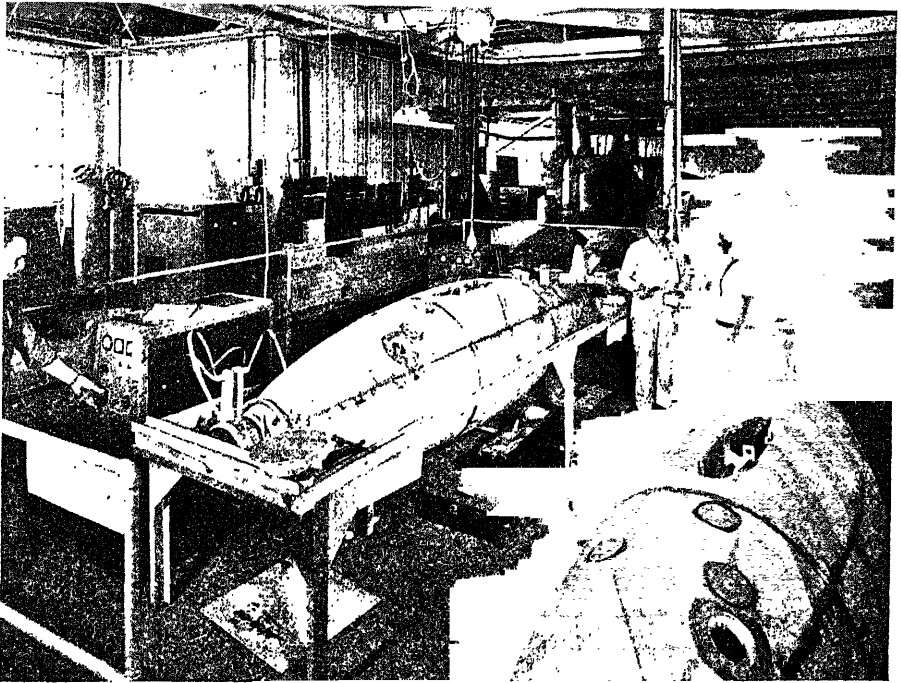


Figure 56. H. F. gluing of droppable fuel tank for aircraft. (Courtesy Gillespie Furniture Co.)

the speed at which full strength is developed, but also in the fact that there is a minimum disturbance to the moisture equilibrium, because the heat is concentrated at the glue line, and not necessarily through the mass of wood. It is further possible, that in curing large areas, spot gluing may be accomplished at a few strategic points, involving a procedure comparable to tack welding. Enough points are selected to insure that the glue will maintain pressure, and then the assembly allowed to cure of its own accord, and develop full strength throughout the entire glue line. As one example of high frequency heating, reference may be made to Figure 56. An end

cap is being rapidly cured to a fuel tank assembly by high frequency. The spacing from the electrodes is quite thick, and curing by thermal conduction would be impractical. High frequency heating and curing of glue lines appear to be well adapted to structural components in building construction, and the attachment of ceiling and wall insulating components. Assemblies may be completed out in the field in a relatively short period of time, and through high frequency the processes of prefabricated construction speeded.

The following table may be considered as representative of the time and the temperature requirements for a hot press phenolic bonded plywood. Data are taken from a publication by the manufacturer of a phenolic resin film ("Tego" film)<sup>34</sup>. The time factors indicated are the minimum required for obtaining water resistant bonds, while 20 to 30 per cent longer time would be best for realizing maximum wet as well as dry strength in the test of the resulting plywood.

Bonding Schedule for Phenolic Resin Film\*

Plate Temperature (F°) Depth to Furthest Bonding Line	Time in Minutes Under Full Pressure								
	1" core			1 1/2" core			2" core		
	280	300	320	280	300	320	280	300	320
1/8"	5	3	3	5 1/2	3 1/2	3	7	5 1/2	4 1/2
3/16"	5 1/2	3 1/2	3	6	4	3 1/2	7 1/2	6	5
1/4"	6	4	3 1/2	6 1/2	4 1/2	4	8	6 1/2	5 1/2
5/16"	8	6	5	8 1/2	6 1/2	5 1/2	10	8 1/2	7 1/2
3/8"	10 1/2	7 1/2	6	11	8 1/2	7	12	11	9 1/2
1/2"	13	10	8	13 1/2	11	9	15	13 1/2	12
5/8"	—	13 1/2	11	—	15	12	—	17 1/2	16
3/4"	—	18	15	—	19	16	—	22	20

\* Moisture content of veneers 7-12%—Specific pressure 150-200 psi 16 gage aluminum cauls.

The above bonding schedule represents only the time the veneers are under full pressure, and do not take into account the assembly and disassembly time. These periods may be quite long unless adequate equipment is available for rapid loading and unloading. The benefits of multi-opening presses for simultaneous bonding of a large number of plywood sections are obvious in lowered production times per panel.

The actual time required for bonding under heat and pressure is, of course, determined largely by the adhesive employed, and the manufacturer of that product should always be consulted. Thermosetting resins must be converted from a fusible soluble state to an infusible, insoluble state and time for this interval is entirely dependent upon the chemical nature of the adhesive and the presence of modifying agents. Too rapid a setting may not always be desirable if the adhesive is susceptible to deterioration

when subjected to high temperatures for an excessive period of time (overcure). On the other hand, if the properties of the plywood assembly are not critically dependent upon the time of cure, a fast setting adhesive is preferred. The outermost glue lines cure first, followed by the innermost glue lines, and while the innermost glue lines are curing the outside glue lines are not adversely affected. With respect to adhesive properties, it must always be remembered that the more advanced the stage of cure of the thermosetting material, the less flow it will exhibit under heat and pressure, and in storage the more readily it may be converted by extraneous influences.

### Plywood Manufacture

An outstanding example of the application of resin adhesives is in the manufacture of plywood—an operation which consumes the major portion of adhesives. While in the preceding paragraphs the common problems arising in the bonding of all woods were discussed, specific attention will now be given to plywood problems. The first development of plywood has undoubtedly been lost in the depths of antiquity, though the attractively veneered furniture coming up through the centuries bears mute witness to its early origin. As a structural material, the cross-bonding of wood veneers was the subject of a patent as early as 1865. A portion of this patent is reproduced herewith in Figure 57 to illustrate the early uses contemplated for plywood<sup>35</sup>. It will be noted that Mayo specifically refers to conduit for water and roofing material in his patent. Naval and building constructions are also suggested. Many important developments have taken place in the plywood field during the intervening years, both in the selection and preparation of wood veneers and the development of adhesive materials.

Wood veneers selected for plywood construction are either peeled from a rotating log (rotary cut veneers), or else sliced vertically parallel to the grain (vertical sliced veneers). For maximum strength, considerable care is taken in selecting a straight grain veneer, the slope deviation of which is generally smaller than 1 part in 15. This is quite important because it has been shown that the modulus of rupture, modulus of elasticity, impact strength, etc., fall off quite markedly when the slope deviation is more pronounced than 1 part in 15<sup>36</sup>. These standards have been written into various aeronautical specifications, which have been most exacting in the selection of veneers for plywood. As some indication of the relationship between the slope of the grain, and the species of wood, an average of the results for Sitka spruce, Douglas fir, and white ash are shown in the table below<sup>36</sup>. In the selection of veneers for furniture or decorative purposes, wood defects such as knots, burls, knurls, etc., are desired for face plies,

# UNITED STATES PATENT OFFICE.

JOHN K. MAYO, OF PORTLAND, MAINE.

IMPROVED MATERIAL FOR ROOFING, TUBING, TANKS, WAINSCOTING, BOATS, AND OTHER STRUCTURES.

Specification forming part of Letters Patent No. 51,235, dated December 26, 1893.

*To all whom it may concern:*

Be it known that I, JOHN K. MAYO, of Portland, in the county of Cumberland and State of Maine, have invented a new and useful improvement in the Manufacture of Material for Structures Generally; and I do hereby declare the following to be a full, clear, and exact description of the same, reference being had to the accompanying drawings, which are made part of this specification, and in which—

Figure 1 is a transverse section of a water-pipe constructed according to my invention, and Fig. 2 is a longitudinal section of the same. Fig. 3 is a side elevation and sectional view of a portion of clapboarding made upon my improved plan. Fig. 4 represents similar views of a section of roofing illustrative of my invention. Fig. 5 represents similar views of a portion of the interior lining of a house or other analogous structure embodying the same principle. Fig. 6 represents a barrel, to which article my invention may also be advantageously applied.

The scale used in the ensuing description consists of a thin layer of wood cut from a board or log and forming a veneer.

My invention consists in cementing together a number of these scales or veneers with the grain of the successive pieces running crosswise or diversely. A number of these scale-boards, their surfaces having been previously treated with cement or analogous material, are so laid together as to cross the grain of the respective pieces, so as to form a firm material for the construction of houses, boats, ships, tanks, floors, pipes, drains, sewers, packing-cases, boxes, barrels, sidewalk-cars, pails, tubs, firkins, measures, cheese-boxes, trunks, valises, dry-docks, canal-locks, mill and factory plumes, masts, spars, outside covering and inside finish of houses, stores, shops, depots, and warehouses, fences, covering of piles, railroad-cars, railroad and suspension bridges, railroad tracks and sleepers, wagons, carriages, and carts, bedsteads, sacking, mattresses, and covering of beds, sofas, and sofa-bedsteads, divans, lounges, chairs, and settees. In house-

architecture the weather-boarding and inside finish of the house may consist of this material, and in vessels of every kind it may be made the covering or lining of the ribs or skeleton, or in some instances may form the body of the article—as, for instance, in pipes in which the layers are united by an impervious cement, and so applied to each other that the grain of one will be lengthwise of the pipe, of another will be at right angles to the former, and, if others are added, may be spirally around it.

By the well-known processes of wet and dry heating such a scale-board may be given to the layers as to permit them to readily assume various figures, or be laid upon irregular objects with the grain of the respective pieces turning diversely, so as to prevent splitting.

I cannot pretend to anticipate all the various uses to which this scale-board may be applied; but suffice it to say that by the means employed, I am enabled to make a very strong and light structure of whatever shape it may be, or for whatever purpose it may be designed. It is capable of being made an effective and elegant substitute for the usual covering of the walls of rooms. For flooring it is also available, and especially in cases where it is an object to make apartments airtight, as in cell-houses, trunk-chambers, and other rooms which it is desired to isolate for any purpose.

It is believed that the drawings in connection with the above statement will suffice to explain my invention without dwelling further upon it.

Having thus described my invention, the following is what I claim as new and desire to secure by Letters Patent:

The application of scale-boards or veneers in layers, the direction of whose grain is crossed or diversified, and which are connected together, forming a material for the construction, lining, or covering of land and marine structures.

JOHN K. MAYO.

Witnesses:

C. D. SMITH,  
JAS. L. EWING.

Figure 57. Early patent on manufacture of plywood.

though a more uniform veneer is selected for the core ply. Each species invites its own particular problem, and the plywood manufacturer can apply adhesives more satisfactorily through examination of wood tech-

nology, particularly the data which appear in various government laboratories.

Average for 3 Species Slope of Grain	Percentage Decrease in Strength Properties as Compared to Straight Grain Wood		
	Flexural Strength	Flexural Modulus of Elasticity	Impact Bending (Max. Drop)
1:25	4%	3%	5%
1:20	7	4	10
1:15	11	6	19
1:10	19	11	38
1:5	45	33	64

The strength properties of the woods are also related to their specific gravity and as determined(<sup>4</sup> page 37) in tests upon 163 native species of wood, the following approximate relationship holds:

$$F_1 = 16,700 G^{1.25} \quad F_1 \text{—fiber stress in psi at elastic limit in bending}$$

$$F_2 = 8,750 G \quad F_2 \text{—fiber stress at elastic limit in compression parallel to grain}$$

$G$ —specific gravity, oven dry

The above formulas indicate the relationships between physical properties and the specific gravity of the wood species. In an analysis of various native species of wood suited for the manufacture of high grade aircraft plywood, the following species were divided into three groups on the basis of their mechanical characteristics and density<sup>37</sup>, and may be considered for face plies:

*Group 1*—Beech, birch (sweet or yellow), hard maple.

*Group 2*—American elm, red gum, mahogany, sycamore, Douglas fir, Black walnut, maple (soft).

*Group 3*—Basswood, Spanish cedar, fir, western hemlock, eastern white pine, spruce, yellow poplar, redwood, sugar pine.

The shear strength developed at the glue line will, of course, become progressively weaker, as Group 1 veneers are compared with those of Group 2 and 3. The Army-Navy Aeronautical Specification for producing flat panels with thermosetting synthetic resin adhesives<sup>38</sup> indicates the permissible test strength values for each group of woods listed above. These values are reproduced in the table on page 378.

The values in the above table are minimum values and typical grades of high quality veneers have no difficulty in meeting these specifications. Birch plywood, for example, averages between 500 to 550 psi shear strength.

**Advantages of Plywood.** To recognize the reasons for the development of plywood, one has only to examine the chief drawbacks of wood. Low cost, abundance, and high strength are the assets of solid wood, though the

No. of Plies	Panel Thickness and Tolerance (in.)	Plywood Shear Strength—Minimum Test Values							
		Group I and/or II with Group III		All Plies Group I		All Plies Group II		All Plies Group III	
		Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
3	0.035-0.004	—	—	300	210	—	—	—	—
3	0.070-0.007	250	150	390	300	310	220	240	140
3	0.100-0.008	250	150	400	310	310	220	230	130
3	0.125-0.010	240	140	380	290	300	210	220	120
3	0.155-0.011	240	140	380	290	300	210	230	130
3	0.185-0.012	240	140	380	290	300	210	230	130
5	0.160-0.012	260	160	410	320	320	230	250	150
5	0.190-0.015	250	150	390	300	310	220	240	140
5	0.225-0.015	240	140	380	290	290	200	240	140
5	0.250-0.015	250	150	390	300	310	220	240	140
5	0.315-0.015	240	140	380	290	300	210	230	130
5	0.375-0.018	240	140	390	290	310	210	230	130

strength in cross-grain is only a small fraction of the strength parallel to the grain. Dimensional stability is poor and swelling cross-grain is quite appreciable. By laying up the veneers so that the grain runs cross-wise in alternate plies, the properties are made more uniform and swelling is reduced to a small fraction of the solid wood (cross-grain). The shrinkage depends upon the species, though from the soaked to oven dry condition, the shrinkage averages about 0.45 per cent parallel to the face grain and about 0.67 per cent perpendicular to the face grain. In order for a plywood panel to retain its form for changes in moisture, it must have a balanced construction, which is obtained by using an odd number of plies, so that there is a parallel ply of the same thickness and same species on the opposite side of the core and equally removed from the core. In plywood construction with many thin plies, the glue joints are less likely to fail than plywood constructed with a smaller number of thick plies.

Stability in dimensions and greater uniformity in physical properties are important benefits accruing from the usual plywood, though for maximum stability, resin impregnated face plies, or thin resin impregnated papers laminated to the face offer outstanding improvements in resistance to moisture. Norris has analyzed plywood construction from a physical stress standpoint, and has reduced to mathematical form numerous formulas for computing stresses under different conditions of balanced and unbalanced plywood<sup>39</sup>.

**Selection of Glues for Plywood.** There are hot press and cold press plywoods, with activities in hot pressing commencing largely with the synthetic resin adhesives in 1935. Prior to this time, hot press albumin types were employed, though not to an appreciable extent, and the number of plywood

presses equipped with multi-opening steam-heated platens were very limited. Various animal and protein adhesives have always been employed for plywood for interior use, where the moisture content is not likely to be high or changed too abruptly. For example, soya bean protein adhesives have been and still are economical adhesives, employed extensively in the manufacture of much of the interior grade of Douglas fir plywood. On the other hand, synthetics are preferred for outdoor use and in regions of high humidity, as they alone are capable of withstanding mold and fungi attack. While various chemicals have been added to the protein adhesive to reduce the tendency toward mold and fungi attack, they are still not equivalent to thermosetting synthetic resins such as phenolics and ureas. Resorcinol formaldehyde could also be considered from a quality standpoint, though its higher cost limits it to secondary bonding operations, often conducted at reduced temperature. With developments in metal-clad plywood, we will undoubtedly see still further types of adhesives employed in plywood manufacture. Owing to the absence of porosity in the metal, the synthetic rubber type of adhesive may be used to establish a prime coat on the metal. To this may be bonded a thin layer of wood veneer, followed by the usual adhesives in assembling to other veneers. Thus veneer faced metal sheets may be handled in assembly gluing operations.

Many articles are formed from finished plywood, such as chair seats, requiring simple curvatures. The preparation of the plywood for this operation generally entails steaming to soften the construction. The synthetic resin bonded plywoods will not open up and delaminate in the presence of the steam. When the plywood has been properly steamed, it is placed under pressure, and formed. The forming pressure is maintained until the high moisture content has been eliminated.

In selecting an adhesive for plywood manufacture, there are many characteristics of the adhesive which should be amenable to the plywood operations. In particular, the adhesive should not lose its effectiveness at the maximum or minimum assembly period for the plywood. Where many units are involved, it is much more expedient to treat many veneers with the adhesive in one operation, storing them until they are ready for pressing. The hot setting synthetic resin adhesives have long assembly periods—several days for some hot press phenolics. On the other hand, the cold or room temperature setting types seldom are effective beyond 30 or 45 minutes at the most, and if parts are not pressed together in this time interval after application, they will not bond well. For large scale production of plywood, the cold or room temperature setting synthetics do not possess sufficient open assembly periods. In earlier chapters methods were suggested, particularly for the melamines and urea resin adhesives, of applying the activating agent to one face and the glue to another face; this involves

extra labor and care, which are not practical in plywood manufacture, particularly when single coating adhesives are available.

The adhesive employed will also influence subsequent operations on the plywood. Synthetic resin types with high solid content will not disturb the moisture balance in the veneers too much, but animal, protein, and vegetable adhesives will add considerable moisture to the plywood, necessitating a drying operation. Large plywood redriers, operating at temperatures of 110 to 120°F maintain a humidity of 40 to 50 per cent during drying. Typical volatile contents in adhesives are as follows:

Adhesive	Typical Solids per 1000 sq. ft. (pounds)	Typical Volatiles per 1000 sq. ft. (pounds)
<i>Cold Press</i>		
Animal and Vegetable	30	60
Casein	25	50
<i>Hot Press</i>		
Urea	20	15
Phenolic	10	15

The above figures are only general and in estimating the amount added to the wood veneers, it must be recognized that a substantial proportion may evaporate before the parts are pressed together. Some of the hot pressed phenolics, and more usually the ureas, are furnished in a dry powdered form which is added to water, or water-alcohol mixtures, before application. Longer open assembly periods are usually claimed for the water-alcohol combinations. Fresh batches are prepared every few hours and added to the glue spreader. This means that some knowledge of the pot life of the glue after mixing is important. Most glues when made ready for application will not last indefinitely—from a few hours for some of the synthetics to 24 hours for some of the animal glues. The exact guide is determined from the viscosity-time curve, and when the viscosity gets too high to be uniformly and evenly applied by glue spreaders, the pot life may be considered at an end. All manufacturers urge that the glue should not be thinned out; otherwise, the desirable strength characteristics will not be attained.

**How Glue is Applied to Veneer.** The most common way of applying glue to wood veneer is by the use of a glue spreader, illustrated in Figure 58. The workman is passing the veneer through the rolls which apply the desired amount of adhesive before the veneer is stacked for pressing. Double glue spreads are recommended for highest quality joints, and for the more porous or rough finished woods. However, for the more common three-ply construction, both sides of the center ply are generally spread at the same time, and the two face plies, untreated, assembled and pressed about the center core.

The glue or adhesive may also be sprayed to the veneer from a spray gun—though this method is usually reserved for uneven shapes. More uniform glue spreads are possible with the machine spreader. Uniform results can, however, be obtained with resin films which are interleaved between the veneer layers at the time of assembly before placing them into the press. Such films are however, usually too brittle for contour or curved sections, which rely on sprayed applications.



Figure 58. Workmen spreading veneers with liquid type resin adhesives prior to laying up for hot pressing.

**Pressing Conditions for Plywood Panels.** Plywood manufacturers must also recognize that recommendations for curing adhesives and developing maximum strengths are dependent upon the maintenance of correct functioning equipment. Steam-heated platens on hot presses will develop "cold" spots if there is not adequate provision made for removal of condensed water. Steady, uniform pressures during cure are essential, particularly to follow up the compression of the wood as pressure is applied. While one can be certain of best results by chilling the platens to some extent before removing the plywood panels, hot removal is also feasible if care has been taken to eliminate accumulated moisture, which, as exploding steam, will tend to rupture the outermost fibers of the wood. A slight breathing,

or relief of pressure, shortly after closing, often proves to be a practical way of providing for the steam and volatile removal. The pressure should not be released too quickly at the end of the cycle.

Cold pressing of plywood involves stacking many layers of resin treated veneers and maintaining pressure until it is safe to remove them, without incurring rupture or delamination of the glue lines. There have been some cold press adhesives designed for plywood and for maintaining a pressure of about 6 hours, before release. However, the majority are kept under pressure overnight. A simplified sequence of operation appears on the chart on

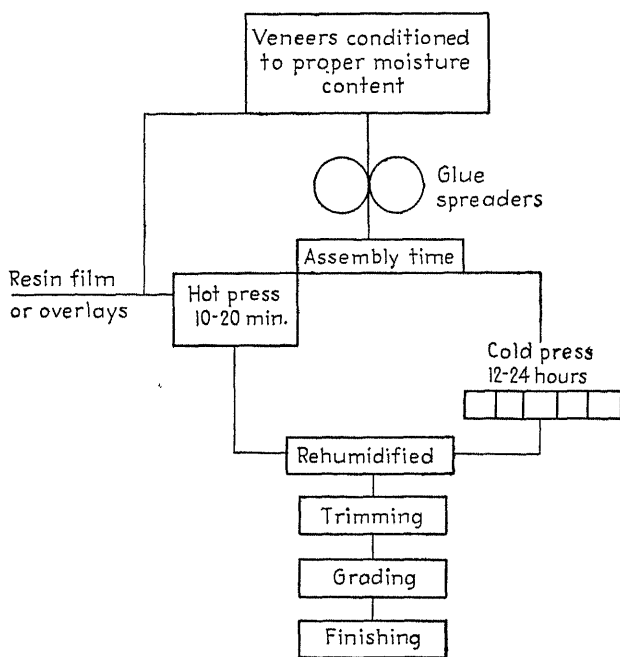


Figure 59. Flow chart for plywood.

the accompanying page. The phenolic resin films, it will be noted, are applied just prior to the hot pressing operation. These films have long storage life and are cut to size to match the plywood panels. Resin impregnated paper or cloth overlays are also applied to the assembly before placing into the hot press.

Good heat conducting cauls such as those made of aluminum are employed for equalizing the pressure distribution. However, when panels are sanded, thickness tolerances can be held closely. Not all are sanded, however, for economy reasons. The plywood panels are trimmed to size—typical of which is 8 feet by 4 feet—the thickness depending upon the number of veneers and their individual thickness.

**Where Plywood is Used.** The applications of plywood are unlimited—in building construction, naval, aircraft, and industrial uses. Plywood built-up beams are in the process of development and practical tests indicate close approximation of results anticipated from calculations<sup>40</sup>. Strain gaging conclusively indicates that the beams act as integral units until the ultimate strength of either the wood fiber or the glue joint is reached. Scarfed assemblies sloped one in twelve can be expected to take their full design stress. For best quality construction, a synthetic resin bonded plywood is recommended.

Some of the more important applications of plywood are in the molded or curved plywood forms described in the next section. Flat plywood panels are used on the inside or outside, depending upon the nature of the adhesive bond. In comparing the manufacture of a number of plywoods with synthetic resin adhesives, Van Eppe points out that the cost of adhesive per 1000 square feet averaged \$3.50 to \$5.00<sup>41</sup>. On the other hand, in evaluating aircraft materials Wallace points out that plywood manufacturing costs are \$1.00 to \$1.50 per pound; 60 cents per pound for steel tubing; and 50 to 75 cents per pound for aluminum<sup>42</sup>.

Newer developments in plywood will see metal and plastic faced plywood panels used in large quantities. Some of these laminates are described in subsequent chapters. Fireproofing qualities may also be developed in plywood, increasing their value in building construction. Various proprietary materials such as "Abopon" are used and various phosphates or chlorinated hydrocarbons employed to treat wood veneers. Unfortunately many of the fireproofing agents are water soluble and may be leached out.

Perry listed many of the newer developments in plywood applications during the second World War. Included in these were (aircraft) flat and molded fuselage and wing sections; complete hulls, decks and housings, bulkheads and partitions—for assault and landing boats; quartermaster corps and engineer corps ramps and pontoons for bridges; camouflage screens; barracks; cabinets, etc.<sup>43</sup>.

**Special Tests on Plywood.** The strength of the plywood bond, both dry and wet, is generally determined by the strip shear test which is discussed in a later chapter. This test method is applicable to evaluation of adhesives for other assemblies. However, herewith are described a few special tests upon plywoods, which evaluate characteristics dependent upon the glue and the type of wood veneer. Yorgiadis and Robertson studied the dynamic modulus and dampening capacity of plywoods under sustained vibration. Nine different types of plywood were run. Poplar and gum have the same dampening coefficient, with birch two-thirds of this value. Dampening also decreases with decreasing ply thickness. Less dampening is encountered in plywoods prepared at higher laminating pressures<sup>44</sup>.

Tests of unprotected plywood panels subjected to weathering have provided evidence with regard to durability under variable conditions of outside weather exposure. The record of 85 months' performance was reported by Wangaard<sup>45</sup>, and Figure 60 is taken from his report. An equal number of yellow birch, yellow poplar, and Douglas fir panels were included in the test. Three-ply panels were made from 1/16 inch veneer, and five-ply panels from 1/8 inch veneer. Each panel was inspected visually and the

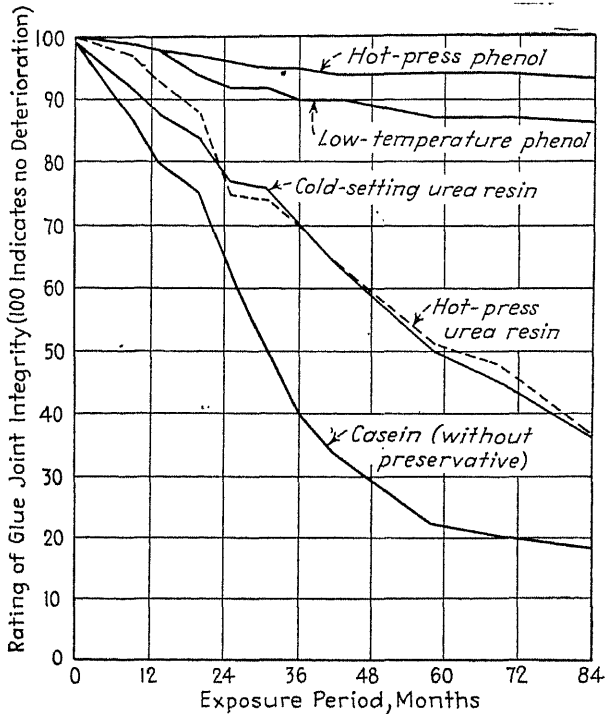


Figure 60. Relative durability of glued joints in unprotected plywood panels subjected to weathering. (Wangaard—Forest Products Laboratory.)

integrity of the glue joint rated on the basis of the open joint area and the percentage of wood failure.

Dietz and Grinsfelder reported on the behavior of phenolic resin adhesives—both film and solution types—when placed under alternating stresses in a cantilever type of machine<sup>46</sup>. The authors concluded the following:

- (1) Fatigue failures are primarily wood failures. The fatigue limit appeared to be about 25 per cent of the static value of the modulus of rupture.
- (2) Alternating bending stresses, including shear stresses up to 200 psi for 100 cycles; up to 125 psi for 10,000 cycles; up to 100 psi for

1,000,000 cycles; and up to 85 psi for 10,000,000 cycles may be expected to decrease the glue line strength of birch plywood not more than 7 to 9 per cent.

- (3) Temperatures as low as  $-70^{\circ}\text{F}$  cause a loss in glue-line shear strength, as well as temperatures of  $185^{\circ}\text{F}$ , though the former were more pronounced in effect.

Kraemer compared plywood bonded with casein and plywood bonded with phenolic resin film<sup>47</sup>. He observed that when the face plies were parallel to the axis of the test piece, the endurance limit in tensile strength was 26 per cent of the static value for both casein and phenolic adhesives. On the other hand, when the face plies were placed at a  $45^{\circ}$  angle to the axis of test, the endurance limit for the resin bonded specimen rose to 52 per cent, while the casein adhesive specimen remained at 26 per cent. Kommers evaluated the endurance fatigue limits of sitka spruce, five-ply poplar plywood, and Douglas fir in bending<sup>48</sup>. Tests were conducted at  $75^{\circ}\text{F}$  and a relative humidity of 65 per cent. The endurance limit for 50 million cycles of reverse stress appeared to be 27 per cent of the static value of transverse strength; with a value of 36 per cent when the repeated stress was in one direction only.

Delmonte and Watkins reported on some creep characteristics of aircraft plywoods comprising three-ply mahogany and three-ply birch faces and poplar cores<sup>43</sup>. The plywood test specimens were loaded as cantilever beams and creep measured as a function of the maximum fiber stress. In addition, warpage due to severe moisture gradients was noted, the mahogany specimens warping quite rapidly.

These tests are only representative of the miscellaneous examinations given to plywood. They are not to be construed as completely indicative of the physical property in question. Variables such as creep and fatigue as functions of glue line thickness would be most informative and data of this nature should be forthcoming in the not too distant future. The effects of extremes of service conditions, involving both humidity and temperature, were never more apparent than during the recent war; many plywood articles suffered deterioration when shipped to the highly humid islands of the South Pacific. The synthetic resin bonded types attained considerable importance under these severe atmospheric extremes. However, protection at the glue line is only one step; it is not a guarantee for the wood veneer. In this chapter the subject of resin impregnation of wood veneers will also be considered.

### Molded Plywood

Molded plywood differs considerably from flat panel plywood in the choice of adhesives, the preparation of wood veneers, and the methods of applying pressure. The techniques of molded plywood, developed largely

during the past several years, owe much of their advance to new developments in synthetic resin adhesives. The field has been nurtured on aircraft and naval problems, though it has begun to make inroads into peacetime pursuits in building construction. The first molded plywood aircraft made its appearance during the late 1930's, and considerable publicity was given to the plastics adhesives employed in its manufacture. However, after the war started, and critical shortages arose in aluminum and steel, a considerable portion of the training aircraft and glider production was undertaken in molded plywood construction. As the aluminum situation eased, the plywood emphasis was withdrawn because of higher cost and service problems, though not before numerous manufacturers acquired much "know-how" in the molding of plywood. Some articles, such as droppable fuel tanks, continued to be manufactured in molded plywood up to the last day of hostilities.

Costs are high for the adaptation of molded plywood to aircraft structures, as a considerable amount of tailoring of the veneer to the contoured structure is involved. However, the strength-weight advantages of the final construction hold much promise, and even in sandwich construction low density balsa cores continue to be featured. It is more than probable that molded plywood will always be an important material in the development of monocoque stressed skin construction.

Any review of the art of molding plywood will of necessity devote considerable space to the methods of developing pressure and expressions such as "Duramold", "Vidal", "Thaden", and others are generally mentioned concomitantly with low pressure plywood molding. Unlike the contact or vacuum pressure laminating of resin impregnated cloth or paper, the forming of plywood into contoured shapes requires greater pressures, because of the greater stiffness of wood veneers. Of course, the pressure requirements depend upon how well the veneers have been cut and tailored to meet the form, though most molding of plywood is conducted at pressures under 125 psi. Molding of plywood is considered a primary bonding operation because the veneers are laid-up with resin adhesives, just as in the manufacture of flat pressed plywood, except that curved molds are employed, rather than flat plates.

**Application of Adhesive.** Most molded plywood forms are produced by hot pressing operations and hot setting adhesives are employed. Phenolic, urea, and melamine formaldehyde adhesives are widely used. The veneers are coated with the adhesive by dipping, roller coatings, brushing, or spraying, the solvent allowed to evaporate, and then placed aside for the laying-up operation. Polyvinyl resins have also been employed in the molding of plywood, though they have not attained the importance of the thermosetting types. Polyvinyl acetate and various acetals have been tried in the

primary bonding of plywood structures, while polyvinyl formal has been utilized abroad in bonding thin veneers together into high density plywood, suited to the manufacture of airplane propeller blanks.

For the bag molding techniques which are described in the following paragraphs, the glues should be dry at the time of assembly, but capable of being softened with heat and pressure, and possessing a long assembly time (more than 24 hours if necessary). The adhesive should soften slowly as the temperature is raised and permit a certain amount of slippage between plies to allow the veneers to adjust themselves to their optimum relationship. Too rapid a flow is undesirable as excessive penetration may occur.

**Techniques of Molding Plywood.** In reviewing the methods of molding plywood, one cannot help but be impressed by the various expedients employed to keep tool costs low and to permit the economical development of pressure over large areas. To obtain adequate and uniform pressure over large areas without the direct utilization of male and female molds, rubber blankets have permitted the application of flexible and fluid pressure over the resin coated veneers. The first part of molding plywood is to lay-up the wood veneers. In production, these veneers are die-stamped to the correct shape so that when placed together they form a contoured shape, mating together properly. Alternate plies are placed at cross-grain with respect to one another, with grain direction predominating on the axis of the greatest stress. To hold the veneers in place as they are placed within or about the form, various temporary expedients can be used. When wooden molds or forms are used, small nails or staples, applied from a hand-stapling machine, may be used. These mechanical expedients hold the veneers in position until the final act of curing the adhesive under heat and pressure. If the mold is of concrete, plaster or metal, a wooden member may be included outside the trim line to permit the attachment of nails or staples, or light weight cheese cloth may be used to keep each layer of veneer in position, the cloth being held by clamps or nails outside the trim line. Still other practical methods include spot or tack gluing of high frequency, which keeps the veneers in position until the assembly is completed and the parts ready to be placed under pressure. In any event, some method of keeping the veneers properly aligned is essential if optimum results are to be realized from the gluing process. All staples or tapes are removed, however, before the final laminating process.

**Fluid Pressure.** The fluid pressure methods are among the most popular techniques for molding plywood. The resin treated veneers are assembled upon a male mold member or punch covered with a form-fitting rubber blanket and placed within an autoclave. Vacuum pressure may be drawn within the bag before placing the assembly in the pressure vessel, permitting the operator to iron out all wrinkles by hand and insure full and uniform

fit of the rubber blanket. After the autoclave has been sealed, initial pressure may be built up by air, followed by the introduction of live steam—generally at pressures of 100 psi. The steam provides the heat for curing the adhesive, and at the same time develops the unit pressure for forming and curing the veneers to the correct shape. When the adhesive has been fully cured, the pressure is released, the autoclave opened and the part removed from beneath the rubber or neoprene bag. This method has sometimes been called the “Vidal” process, though there are earlier counterparts in the rubber industry for molding industrial rubber goods and boots.

Instead of laying the veneers upon a mold, they may be placed within a mold, and an internal fluid pressure applied. This pressure forces the veneers out against the sides of the mold to capture the external details with the utmost accuracy. An inflatable rubber bag is confined within the mold by a pressure plate. Heat may be delivered through the fluid pressure medium, though more usually heating means are incorporated within the female mold—as through electrical resistance coils near the surface of the mold. The mold member may be made of reinforced concrete. The veneers could be preformed and assembled upon a positive male punch before inserting them into the die for final shaping. This process has been referred to as the “Duramold” process, and has been used for shaping large aircraft and naval components such as fuselage or hull sections.

The various methods of developing fluid pressure with the aid of an autoclave or by an expandable rubber bag are illustrated in Figure 61, taken from a Forest Products Laboratory report<sup>50</sup>. The report emphasizes the need for air tight bags which do not leak, otherwise the pressure medium such as steam may adversely affect the veneers and the strengths obtainable in the glues. When carefully handled the bags should last some 30 to 40 cycles. Thin substituted film materials such as polyvinylidene chloride or cellophane did not stand up as satisfactorily<sup>51</sup>.

It is considered desirable in molding plywood to have a glue which slips readily while passing through its fluid stage under heat and pressure<sup>52</sup>. This action permits adjustments of the veneers to a position of least resistance and the elimination of wrinkles in the final molded product. Various glues have been compared upon a steam heated mandrel, and the load required to cause slipping noted at different temperatures. The fluidity of the glue cannot be excessive either, otherwise too much penetration will take place or the glue will accumulate at the edges of the assembly.

*Flexible Pressure.* As distinct from fluid pressure, flexible pressure includes those methods such as the hat mold technique, whereby a punch covered with an inflatable rubber bag is coordinated with a die member. The molds are generally mounted upon a hydraulic press and laminating pressure is derived at the punch as its rubber bag closes down into the

mold. Steam pressure may be admitted into the bag, and may also be used to heat the molds which are often of some cast metal. These operations are often conducted more rapidly than fluid pressure in the autoclave, largely because the time of loading and unloading the die members is reduced. The resin coated veneers are usually laid-up first as a preform of

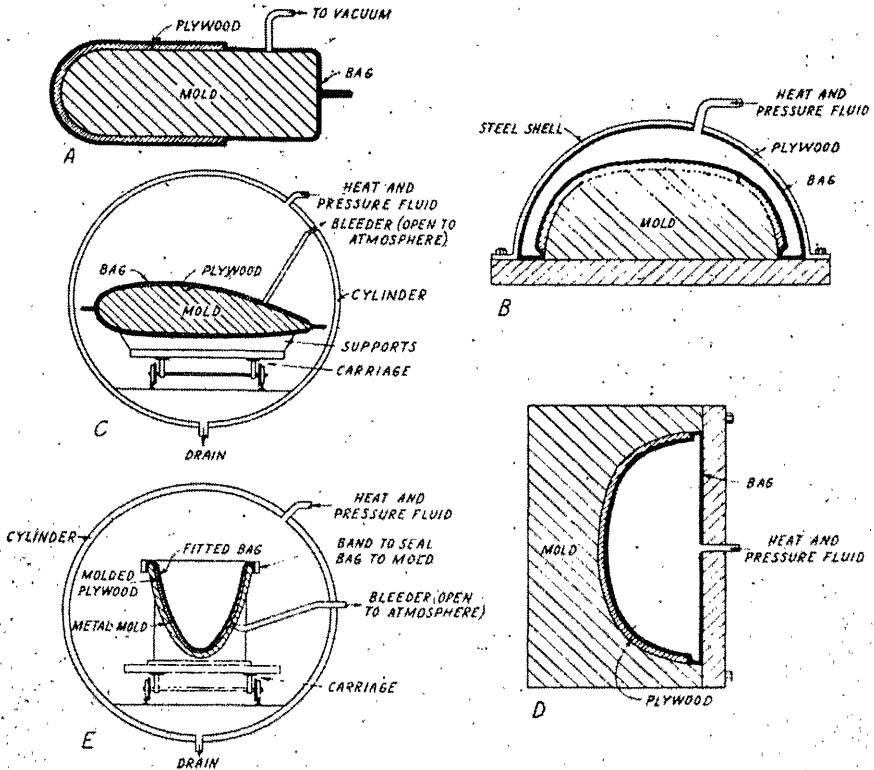


Figure 61. Low pressure methods of molding plywood.

the contour to be reproduced. Greater unit pressures—up to 500 psi are derived by this method.

The various techniques described above lend themselves to efficient assembly methods, as in many instances not only are the plywood skins produced in one operation, but also at the same time some ribs may be molded in, integral with the structure, to give added stiffness. One of the first patents on fluid pressures for veneers within an autoclave was by Teague<sup>53</sup>. Other unusual sections which have been prepared by these methods include the manufacture of plywood tubing with the walls helically wrapped and glued with synthetic resin adhesives. Such tubes have shown

very high strength, durability, and light weight. Tubings with diameters up to 2 feet have been produced<sup>54</sup>. Of course, in all cases the molded plywood shapes require a careful finishing schedule in order to protect the laminates from the ravages of weather. Thin phenolic resin treated papers or cloth applied to the outside plies will develop excellent moisture barriers, it has been pointed out. Otherwise, various sealer coats, followed by finishing coats are necessary to obtain the best results.

### Joining Finished Plywoods

The assembly and union of various plywoods, as through methods of scarfing, progressive gluing, and tapeless splicing, are of fundamental importance because they are directly related to the commercial applications of plywood and because of the specialized adhesive requirements. The purpose of scarfing is to enlarge the size of the sheet maintaining its normal strength without increasing thickness at the joint. Considerable space is devoted to the subject of joining finished molded plywood in the Army-Navy Aeronautical specification on this subject<sup>55</sup>. Thermosetting synthetic resin glues are recommended in specifications for molded aircraft plywood. For edge joints it states: "Whenever practicable, all joints between edges that are parallel to the grain shall be formed by jointing the edges straight and square and securely gluing with a water resistant glue." There are permissible deviations, such as scarfing the edges with a 1 to 8 slope and assembling in the proper relationship. For end grain joining, the scarfing procedures are discussed in greater detail in the paragraphs to follow. Open edge joints are permitted in plywood providing the open joints in successive plies are staggered to prevent any undue reduction in strength. The open joints should not exceed 1/16 inch for any curved section.

End grain joints are best accomplished by scarfing, and no butt joints are permitted in any ply. Scarfing machines are recommended in order to attain any degree of accuracy and good matching of the veneers. About 1 to 10 or 12 slope is generally applied to the scarfed joint. In assembled molded plywood, the scarfed joints in adjacent plies are best staggered a minimum of six inches. The most important step in preparing a scarf joint is the machining of the scarf surface. The mating surfaces should be true, smooth and accurate if a well glued joint is to be realized, with the tip of the scarf slightly blunt and not feather-edged. Planers and jointers should be used for the operation, the veneers being held in proper jigs to insure uniform and accurate machining. Sawing is not recommended for the preparation of a scarfed joint as it will leave too many torn and loose fibers and probably a poor bond.

The scarfing of completed plywood sections offers even greater problems when the scarfed assembly follows a curved pattern, e.g., the manufacture of

droppable fuel tanks from molded plywood. Scarfing machines are designed to swing on a curvature corresponding to the contour to be followed on the body of the tank, and in this manner parts are tailored together to provide a perfect mating. The assembly is effected between the scarfed plywood sections with the aid of resorcinol-formaldehyde adhesives which are set by heat through electrical resistance strips placed in close proximity to the glue line. The glue at the scarf joint should be of the same quality as that employed throughout the body of the laminate. The blunt tip of

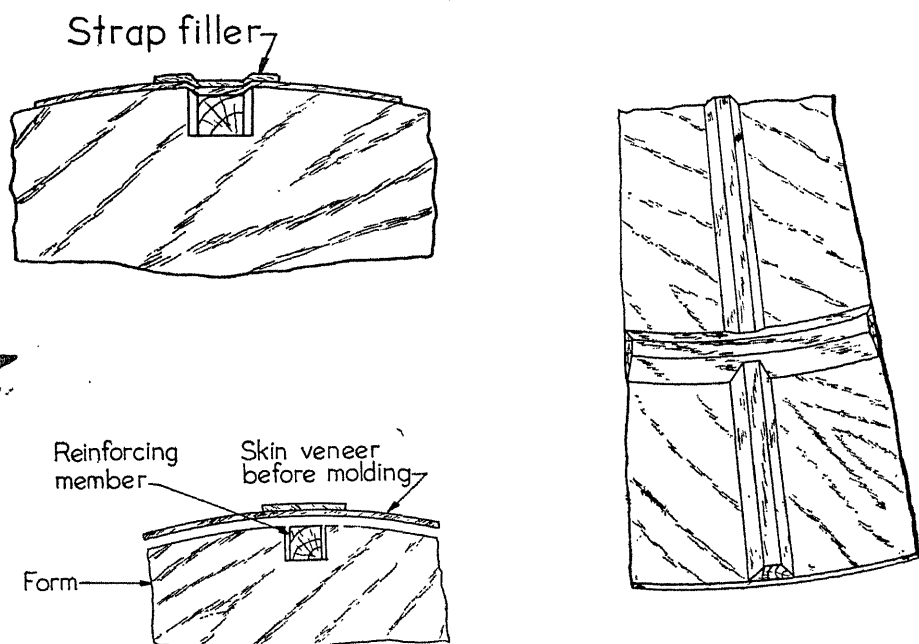


Figure 62. Assembly of reinforcing ribs to molded plywood skin. This may be accomplished at the time of molding the plywood.

the scarf may project slightly beyond the region of assembly, providing it does not project more than 0.01 inch. This is sanded off after the bonding operation is complete. The scarfing pressure should be equipped with adequate clamping facilities to hold the beveled or scarfed surfaces in alignment and prevent any slippage.

As already indicated, the attachment of reinforcing ribs to molded plywood may be accomplished at the time of the molding operation within the rubber bag or in a separate operation at the time the plywood shell is fitted to the frame work for which it was designed. Figure 62 illustrates a typical attachment. The protruding strap veneer filler may be sanded off after

the assembly is complete to give a smooth, uniformly flat surface without humps or depressions. This is rather important to aircraft construction. This type of assembly is adapted to male molds, as the ribs generally fitted inside the skin rather than outside. Another process for manufacture of molded plywood entails laying thin veneers in overlapping relationship to one another. The lapped plywood is molded to shape and finished assembly sanded down to a smooth exterior<sup>56</sup>.

Small repair patches upon plywood construction are frequently necessary in the event of puncture or damage to the plywood. These patches may be circular or square, and beveled between 1 to 10 and 1 to 15. Various accessories may be employed. Burchard, for example, describes a flexible vacuum repair kit which will aid the development of a strong, scarfed patch<sup>57</sup>. With heat, various thermosetting adhesives may be applied.

With interest in prefabricated construction growing all the time, the proper scarfing of plywood assemblies in the field and their assembly into integral components will become quite important. Various diagonal and curved scarfed joints have been proposed in the construction of plywood for maximum efficiency. Doublers glued to the skin are recommended for all severe stress concentrations. The doublers may be some resin impregnated plywood ("Compreg") for maximum strength<sup>58</sup>. Resin impregnated woods however, require greater care in assembly and more careful selection of adhesives, as will be pointed out shortly. Allward has given a good presentation of the basic requirements for plywood in aircraft construction<sup>59</sup>. Anderson emphasized the importance of finishes for plywood in the aircraft industry<sup>60</sup>. He indicated a preference for phenolic coatings over alkyds and cellulosic derivatives. The success of exterior grades of plywood is closely related to the finishing schedules developed for protecting their surfaces.

The size of most hot presses is generally limited and not many are equipped to press plywood greater in size than 8 feet by 4 feet. Consequently it has been necessary to develop progressive gluing methods to make possible the development of very long sections of plywood. One of the most important problems in progressive gluing is to secure an adequate bond for 3 or 4 inches adjacent to the edges of the platen. Perry and Sorenson have discussed the procedures for progressive gluing<sup>61</sup>. For this plywood, not over 1/8 inch thick, canvas covered cauls are recommended to help maintain proper moisture balance and prevent fast overcuring of the adhesive. For thicker plywoods, the conditions are less critical and gluing in half steps are recommended. A section of the plywood is cured in one-half of its normal time, in one-half of the press space. The plywood is advanced to the other half of the press space and the cure completed. Each section is advanced in one-half steps until the complete plywood has been prepared.

Considerable work is entailed as the veneer approaches the press, for seldom are the veneers wide enough so that the face ply is in a single sheet. The veneer goes through a number of clippings (to remove defects), edge jointing and edge gluing operations. The edges of the veneer are trued up on the veneer jointer, and glued together to form a single sheet. The machine for accomplishing this is called a tapeless slicer, and in eliminating the tape formerly required, there is a considerable saving in the cost of producing the plywood. The importance of the operation is shown by the fact that it accounts for one-third of the labor costs of producing three-ply aircraft plywood<sup>62</sup>. In the machine the sheets of veneer are forced against a central fence by converging endless chains.

In concluding this brief review of molded plywood, it may be re-emphasized that the adhesives which have been developed and the special techniques of developing pressure have made possible many curved surfaces which hitherto were considered impractical. Whether these surfaces are for aircraft, naval construction, housing, or various industrial purposes, the plywood would soon lose its appeal of high strength and light weight if modern synthetic resins did not make permanent, durable assemblies feasible.

### Laminating of Structural Timbers

It was pointed out earlier in this chapter that the laminating of structural timbers, as for example in the construction of laminated arches, marks one of the new outstanding contributions of adhesives to the wood industry. The past war has witnessed the development of numerous laminated members for naval and aircraft construction and from these applications much information has been gained which should contribute to the advancement of the art of wood bonding. The Gamble Brothers at Louisville have produced keels for 11,000 landing craft and 100 PT boats. Oak timbers and synthetic resin glues were featured throughout this construction<sup>63</sup>. The Mosquito bombers of the English air force attained an outstanding record for themselves during the last war. An all plywood airplane, they represented an outstanding wood development. The spars were 50 feet in length and laminated with the aid of synthetic resin adhesives. Champion has predicted the mass production of pre-fabricated housing construction with synthetic resin adhesives<sup>64</sup>.

British boat building also featured laminated keels, using synthetic resin adhesives<sup>65</sup>. Wilson prepared a very comprehensive report on glued laminated arches, which have provided much of the background for developments in this field. He discussed the disadvantages and advantages of a glued, laminated construction<sup>66</sup>. Among the advantages were cited the following:

(1) Arches to span large unobstructed areas with superior architectural effect are made possible. An arch involves no intricate framing and is more fire resistant.

(2) Lumber used in developing laminated arches can be dried in a shorter time than heavier structural timbers. They are best dried to the same moisture content as the atmosphere they will be exposed to most frequently.

(3) Members can be built-up to greater lengths and larger cross-sections than individual timbers.

(4) Laminations can be positioned in accordance with their strength characteristics, as determined by species, density, and defects, and gain the advantage of high strength at points where such material is needed.

(5) Glued laminated construction has a record of successful use in Europe for forty years.

(6) Protective films for chemical and weather protection may be laminated as an integral part of the structure.

The following disadvantages are cited:

(1) Rolling shear or tensile factors producing delamination have not been thoroughly explored as yet for laminated constructions.

(2) Skilled workmanship in applying and handling the gluing is essential to the success of the laminated arch.

(3) Economies of this procedure have not been fully evaluated as yet.

While the laminated arch was selected as a classic example, the problems therein reflect upon many of the applications of laminated timbers. Most of the adhesives required for this assembly job are cold setting, though hot setting types are practical if high frequency facilities are available for curing the glue. When the glue lines are far removed from the source of laminating pressure, high frequency curing appears practical. Taylor has presented the subject of the high frequency heating of lumber<sup>67</sup>. The variation of the power factor with percentage of moisture is shown for Sitka spruce and mahogany. There is gain not only in the rate of heating but also in the temperature gradient across the lumber. Russell and Mann have compared parallel bonding to perpendicular bonding (with reference to the plane of the glue line)<sup>68</sup>. They report that in parallel bonding, the field tends to concentrate at the glue line—though for setting temperatures above 212°F, either parallel or perpendicular bonding may be equally effective. When the dimensions of the work become comparable to the wave length of the frequency employed, uniform heating becomes more difficult. Molded wood, resin impregnated propeller blades have also employed high frequency heating to speed up operations<sup>69</sup>. Similarly in the plant of the Formica Insulation Company, laminated wood 52 inches long, 10½ inches wide, and 6¼ inches thick has been bonded with the aid of high frequency fields<sup>70</sup>. Where curved sections are present, the electrodes can be the press

platens (properly insulated), or metal sprayed on a contoured mold. If two laminations are being manufactured, one sheet metal plate inserted at the center, between the 2 stacks of laminations, will serve as one electrode, and the press platens as the other. There appears to be a question on optimum frequency for bonding plywood, some manufacturers finding 3 and 6 megacycles, and their harmonics to be satisfactory. On the other hand, the Federal Communication Commission has allotted limited frequency bands for electronic heating at 13.6 megacycles, 27.32 megacycles, and at 40.98 megacycles. Extensive shielding is usually required for high frequency gluing of plywood.

In addition to the parallel and perpendicular methods of bonding structural timbers, Godfrey and Bilhuber have employed the stray high frequency field, which has been suited to built-up sections such as wings, ailerons, elevators, stabilizers, floors, and the like<sup>71</sup>. Berkness reviewed the possibilities of drying wood with high frequency as well as the setting of the glue line<sup>72</sup>. Another procedure to consider, which has much economical merit, is to set the glue with high frequency at a few limited spots—sufficient to hold the laminations together; then permit the normal processes of cure to convert the entire assembly over at room temperature.

### Resin Impregnation and Bonding of Wood Veneers

In the chapter on synthetic resin adhesives from phenol-formaldehyde, considerable attention was given to the subject of resin impregnation of wood veneers. When the resin has been cured *in situ*, the product has generally been called "Impreg"<sup>73</sup>, though when the assembly has been completed with the aid of heat and pressure, the resin impregnated wood laminate is called "Compreg"<sup>74</sup>. Greatest interest has been shown in "Compreg", both as a complete structural material and in combination with unimpregnated wood veneers. The dual rôle of synthetic resins as adhesives and impregnants for wood will be reviewed briefly and some of the problems of bonding impregnated wood veneers discussed.

Resin impregnation of wood has been viewed chiefly as a wood stabilizing procedure, as the veneer as well as the plywood prepared by this method will swell and shrink much less readily with changes in moisture than untreated wood. The physical properties are increased considerably, though not without an increase in density, and the general observation of the relationship between density of the wood and the physical properties appears to hold for the resin impregnated woods. There are two exceptions, however: with resin impregnation and pressing the shear strength increases much more rapidly than other physical properties; the impact strength becomes less than for solid wood. This decrease in impact strength is dependent to a large extent upon how thoroughly the resin diffuses into the cell wall of the

wood. Adsorption rather than absorption of the resin appears to be the best criterion for maintaining impact strength, though less satisfactory in stabilizing wood against moisture influences.

**Types of Resin Used.** Practically all types of low viscosity resins have been employed for the impregnation of wood veneers. Stamm and Seborg describe phenol-formaldehyde, polystyrene, urea-formaldehyde, and alkyd resin applications to wood veneers<sup>75</sup>, though phenol and urea-formaldehyde alone have attained commercial importance. The writer has experimented with furane resins and with low molecular weight styrene resins in application to wood, but processing advantages appear to lie with the phenolics. Some evidence of resin impregnation was indicated in the manufacture of super pressed plywood by Stern, Perry, and Bernhard, who employed multiple layers of phenolic resin film in the manufacture of high density plywood under laminating pressures of 1000 to 2000 psi<sup>76</sup>.

There has been considerable discussion of the relative merits of water-soluble phenolic resins versus alcohol, medium molecular weight resins for wood impregnation. These discussions may well be based upon the relative merits of adsorption on the wood fiber or absorption into the wood fiber. The Forest Products Laboratory has shown that true resin diffusion into the wood tracheids, is accomplished by diffusion through an aqueous medium into the cell wall. When the cell wall reaches its saturation point (usually with 25 to 30 per cent of resin absorbed), further resin would only fill the lumen and not contribute to stabilization. The employment of water-soluble phenolics for this purpose was a radical departure from the earlier practices of using non-water-soluble phenolics for treating wood, although the amount of resin penetration was questionable. The lower impact strength of water diffused resin techniques, led to the adoption by some manufacturers of alcohol-soluble phenolic resin types, which under laminating pressures were forced into the wood structure. An appreciable stabilizing effect was noted together with the physical property advantages of "Compreg".

There have been other methods more recently developed for stabilizing wood, whereby wood is compressed under sufficient heat and pressure to cause the lignin to flow and relieve internal stresses resulting from compression<sup>77</sup>. This has been found to eliminate the spring-back tendency normally encountered in densified wood. Wood so processed has been called "Staypack", and when laminated with synthetic resins has formed a tough, stable structure. It lacks the mold and fungi resistance of resin impregnated woods, however. In comparing the various methods of improving wood with thermosetting phenolic resins, Klein *et al.* point out that the choice of adhesive or bonding technique depends upon the property to be emphasized<sup>78</sup>. The resin impregnation process prepares the most stable wood with the best appearing surface; the phenolic film process produces a

wood with highest impact strength and most uniform and simple from a production viewpoint; the glue spreading technique of a wet glue is most easily compressed and the lowest in cost.

Casselmann has presented an interesting survey of the properties of birch "Compreg", as dependent upon the nature of the resin impregnant and adhesive<sup>79</sup>. Some of his data appear in the table below. He points out the wide differences between various phenolic resins in stabilizing wood. The water-soluble phenolics are described as falling in the 150 to 200 molecular weight range, while the alcohol-soluble types have average molecular weights of 500 to 1000. He predicts a flexural strength of 48,000 psi and a modulus of elasticity of  $5 \times 10^6$  psi for "Compreg"<sup>80</sup>.

Physical Properties of Birch Compreg (Casselmann)

	34.5% XJ-16235 (plasticized BR-15100)	30% BR-15100 Water-Soluble Phenolic	30% BV-10678 Alcohol-Soluble Phenolic
Specific Gravity	1.32-1.37	1.35-1.37	1.34
Flexural Strength	39,000 psi	39,000 psi	40,000 psi
Modulus of Elasticity	$3.45 \times 10^6$ psi	$3.0-3.6 \times 10^6$ psi	$3.5 \times 10^6$ psi
Izod Impact—ft lbs in notch	7.3	1.4-4.1	6-7.0
Compressive Strength	25,000 psi	25,000 psi	25,000 psi
Water Absorption %	2.3%	1-2%	4-6%

In addition to the various phenolic resins which have been used to impregnate wood, some efforts have been made with urea-formaldehyde resins and melamine formaldehyde resins. While early work at the Forest Products Laboratory indicated that this was possible, it was felt that phenolics could accomplish the stabilization much more effectively. Besides they penetrated into the wood structure more readily. Notwithstanding, there was some effort at commercialization of the urea resin technique. In one process, the dimethylolurea (3 parts) was dissolved and urea crystals (1 part) added. This technique applied to wood produced a hard surface, and more attractively finished material<sup>81</sup>. It is pointed out that by the urea resin treatment poplar, for example, can be made as hard as maple. For impregnating thick sections of wood, vacuum for 10 to 20 minutes, followed by air pressure at 100 psi is recommended<sup>82</sup>.

Instead of using urea resins, urea crystals have been employed to soften wood. The process requires immersion of thick sections of wood into a concentrated solution of urea at a temperature of 130 to 140°F for a number of hours. This is followed by drying out. The wood is then heated to about 350°F at which temperature it is readily bent because of the plasticizing action of the urea. Further continued baking exerts a stabilizing effect<sup>83</sup>.

Polyvinyl formal has been used in Great Britain in the manufacture of high density plywood for aircraft propellers. Presumably under the high laminating pressures, some impregnation of the wood structure is obtained. Treatment of the green logs with phenolic impregnating resins has also been practiced, and there are various patents describing this technique. In one, the resin solution is forced into the log at the end. After the log has been kiln dried, it is converted by the heating into a hard, dense resin impregnated wood<sup>84</sup>. Phenolic resin impregnated high density woods have been used for tools and jigs in both Great Britain and Germany. Young and Palese discuss the molding of resin impregnated woods into furniture, toys, handles, etc. They emphasize the impregnation of thick sections of wood<sup>85</sup>. Evaluation of the impregnation of resins into thick sections of wood is possible through various hardness tests, whereby the rate of penetration of a hardened steel ball into the surface of the wood is examined<sup>86</sup>. A piece of wood with a well impregnated cured resin will require much greater force to penetrate than an untreated wood.

**Method of Securing Resin Penetration.** The method of securing resin impregnation depends to a large measure upon the type of resin to be used. Water-soluble resins diffuse into the wood structure and cell walls through the medium of water. Relatively long diffusion periods are required. On the other hand, non-water soluble resins are introduced by mechanical action, usually through pressure. Temperature as well as pressure will aid this impregnation.

For very thick sections, vacuum-pressure systems are the most effective. This technique is a carry-over from the art of creosoting telephone poles and railway logs. It is effective however, in forcing the resin into the structure. Generally 1/16 inch veneer thickness is considered as the dividing line between choosing simple immersion and diffusion at atmospheric conditions or the use of vacuum, followed by pressure.

**Preparing "Compreg".** Heat and pressure are employed to prepare the resin impregnated, compressed wood. While enough resin may exude to permit bonding of adjacent layers of wood veneer, best results and highest shear strengths are obtained with a non-penetrating thermosetting adhesive at the glue line, which is in addition to the impregnant in the veneer. Before pressing, the wood should be conditioned so that excess moisture is removed and low molecular weight resins are partially converted by preheating. This is important, otherwise the high laminating pressures of 1000 to 1500 psi will cause the volatiles to flow and cause a rupture of the wood structure. Up to 30 per cent of phenolic resin is generally employed, the amount being determined by the fiber saturation point of the wood structure. Up to this range of moisture the physical properties of wood fall off quite appreciably. However, beyond about 30 per cent of

moisture, the additional water fills the lumen without detracting from the strength of the material. In replacing the water with resin, advantages are registered largely during the impregnation of 30 per cent of resin. Beyond that point, the stabilizing effects of additional resin are of less consequence.

**Cementing "Compreg".** The bonding of resin impregnated compressed wood offers many problems, as it is not readily cemented by those adhesives commonly employed for wood. More often the adhesive preferred is the same as may be employed in bonding laminated phenolic paper or canvas base. Best results are obtained by sanding the surface of "Compreg". Both furane resin adhesives and resorcinol formaldehyde adhesives do an excellent job in cementing resin impregnated wood. Animal, casein, and vegetable adhesives do not bond "Compreg" satisfactorily. In a series of investigations it was determined that acetone, benzene, or alcohol wash or acid or alkali pre-treatment did not materially affect the shear strengths obtained<sup>87</sup>. Hot and cold setting phenolic and urea adhesives were compared in a preliminary study. Under assembly pressures of 300 to 450 psi, shear strengths up to 900 psi by the strip shear tests were obtained for a number of phenolic and urea adhesives, generally acid-catalyzed.

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## Chapter 16

### Cementing of Organic Plastics

The cementing of organic plastics materials has been of the utmost importance in the fabrication and assembly of various plastics into miscellaneous articles. The problems of adhesion and the selection of the adhesives for these materials differ appreciably from those encountered with wood. In the first place, the organic high polymers in molded, laminated or cast forms are relatively non-porous as compared to woods. One cannot depend upon as rapid diffusion of volatiles through the polymer unless there is a definite chemical compatibility. When solvents diffuse through the polymers, the weakening effect on the structure is quite pronounced. In choosing the right adhesive for bonding organic plastics considerable attention should be given to the chemistry of the materials being bonded and the chemical nature of the cementing agent. Therein lies an important difference between wood bonding agents and plastics bonding agents—the majority of wood adhesives are water- or water-alcohol-soluble; while the majority of cementing agents for plastics are organic solvents alone or in combination with other materials.

The cementing of organic plastics may be divided into three main groups:

- (1) Cementing of the plastic to itself—as in the assembly of fabricated pieces to form a whole, integral unit.
- (2) Cementing of dissimilar plastics materials to one another.
- (3) Cementing of organic plastics to non-plastics.

In this chapter the two first groups will be discussed, while the cementing of plastics to other materials—rubbers, metals, woods, papers, and plastics—will be covered in other chapters.

#### Cementing of Thermoplastic Plastics to Themselves

The cementing of the plastic to itself may be further subdivided between the cementing of thermoplastic and thermosetting materials. The problems are basically different, as well as the choice of adhesives. Any study of the cementing of thermoplastics will of necessity be accompanied by considerable study of solvents and solvent combinations, as the two fields

are inseparable. Solvents act as agents in cementing the thermoplastics. By themselves, solvents are generally volatile, possessing little or no pronounced adhesion to chemically incompatible substances. As adhesive agents, however, solvents promote the welding of one portion of the plastic to another by serving as the medium in which the high polymers possess a certain degree of freedom to adjust themselves to those favorable molecular arrangements for securing good bonds. Once favorable molecular arrangements have been established, however, the solvent has served its usefulness and its elimination should follow as soon as possible. The retention of the solvent reduces the strength of the plastic and the strength of the assembly.

In the earlier chapters on adhesives from various thermoplastic materials considerable space was devoted to the subject of solvents for various plastics, and much data presented on the viscosity of various thermoplastics in solution. In the following table, representative solvents and cementing agents for each of the major thermoplastics are cited. While formulations will be discussed a little later in which the high polymer is dissolved in a solvent and as such is sold as a cement, the table herewith is intended for those operations in which a small amount of solvent is introduced directly between the joints to be cemented. A surface dissolution occurs and a welding together of adjacent sections of organic plastics takes place.

Assembly Operation	Representative Solvent Cementing Agents
Polystyrene to polystyrene Polyvinyl butyral to polyvinyl butyral Polymethyl methacrylate to polymethyl methacrylate	Benzene, toluene, acetone Isopropyl alcohol, furfural Ethylene dichloride, chloroform, glacial acetic acid, methyl methacrylate monomer
Cellulose acetate to cellulose acetate	Acetone, methyl ethyl ketone, nitromethane, chloroform
Cellulose nitrate to cellulose nitrate	Acetone, methyl ethyl ketone, ethyl acetate, butyl acetate
Cellulose acetate-butyrate to cellulose acetate-butyrate	Acetone, chloroform, ethyl and butyl acetate
Polyethylene to polyethylene	Difficult—Hot xylene and toluene
Polyvinylidene chloride to polyvinylidene chloride	Difficult—No effective solvent
Polyvinyl chloride acetate to polyvinyl chloride acetate (copolymers)	Isophorone, mesityl oxide, acetonyl acetone, cyclohexanone
Polyvinyl acetate to polyvinyl acetate	Acetone, methyl ethyl ketone, methyl acetate
Ethylcellulose to ethylcellulose	Acetone, benzene (80)-alcohol (20)
Polyamide to polyamide	Difficult—Hot formic acid or hot phenol

**Factors Influencing the Application of the Solvent.** There are numerous factors influencing the practical applications of the solvent cementing agents. The surfaces to be joined should of course be free of all foreign matter, as far as practical. This generally means wiping dirt and grit off with a clean rag, using perhaps some soap and water. When thoroughly dry the solvent may be applied. The amount of solvent required is determined by how well the thermoplastic surfaces mate or fit together. If the fit is poor and considerable gap is present, the surface may have to be wetted with the solvent at length. In some instances, complete immersion is recommended until the high points are softened sufficiently to be pressed out when the surfaces are placed together. Long immersion in the solvent cementing agent is, however, not recommended when it can be avoided, because the longer the immersion, the greater will be the pick-up of the solvent and the longer the time for the solvent to evaporate and permit full strength to develop.

Close fitting joints are recommended under all circumstances as the solvent will be at a minimum and the strongest assemblies can be effected. The usual fabrication procedure is to place the sections together in their proper fashion, mask off the glue or assembly line with a tape unaffected by the solvent to be used, and lightly touch a few drops of the solvent to the glue line. It will quickly disperse between the sections by capillary action and rapidly wet the surfaces to be joined. Rapid and efficient cementing can be conducted in this manner. For the more rapid evaporating solvents, a slight pressure for a few minutes will suffice to hold the assembly together. Pressure from the hand may be sufficient if just an edge is being glued, though if larger sheets are being joined, a more positive clamping device is preferable.

Typical fabricated assemblies completed by solvent cementing operation are illustrated in Figure 63, which demonstrates a model fabricated acrylic plastic house complete with furniture and completely cemented together with solvent cements such as chloroform and ethylene dichloride. Many industrial and machine models have been prepared in a similar manner—in fact, one of the attractive features of working with sheet stocks of thermoplastic materials is the ease of assembling the components after all the machine work has been finished. These solvent cementing operations are invariably conducted at room temperature, and with only slight unit pressure.

**Crazing.** One common complaint about solvent cementing agents for thermoplastics is the tendency for crazing to occur. This defect is more apparent when transparent thermoplastics are being assembled, though it may also prevail in opaque joints. A contributing factor to the formation of craze marks is the presence of stresses at those regions of the parts being

assembled. The stresses may have been caused by severe machining operations or drawing operations on the thermoplastic member. In course of time these craze marks may progressively grow worse, and as focal points of stress concentration, result in a mechanical failure if severe loads are to be carried. Annealing of the joints by heating and slow cooling will relieve the internal stresses, though this may be damaging to the design and dimensional details of the fabricated object. The best preventive measure is to machine and finish the joints slowly and carefully,

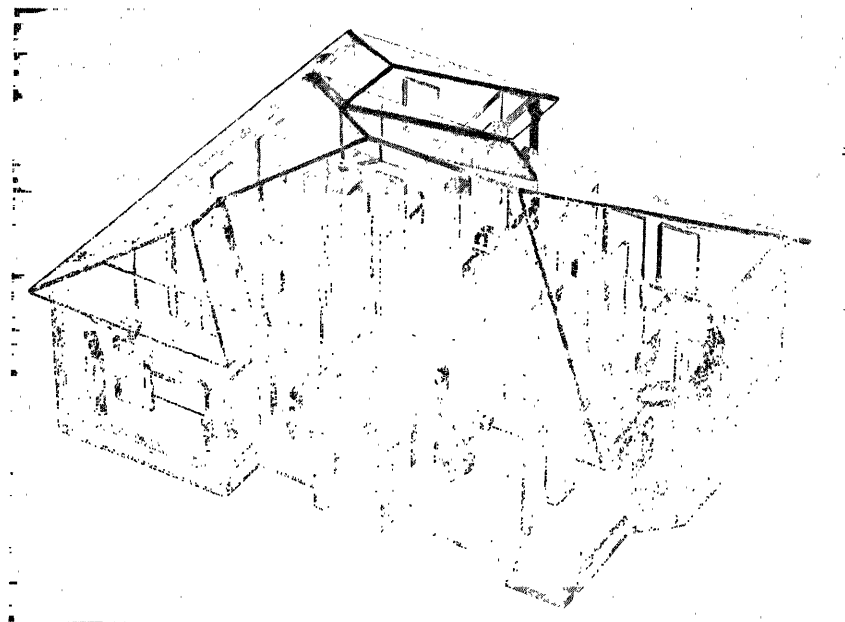


Figure 63. Transparent model house and furniture prepared from acrylics and cemented by solvents.

avoiding rapid and severe machining operations which tend to create stress.

Drilled holes and routed edges are difficult subjects and some crazing generally occurs in cemented assemblies of these members. Cemented assemblies of this character may be encountered in the fabrication and assembly of transparent enclosures for aircraft, where long curved reinforcing strips may have to be cemented to a curved transparent enclosure. Even the liberal application of partially polymerized methyl methacrylate does not eliminate the crazing in drilled holes in acrylics, though more crazing is evident when the lower viscosity monomer is employed.

**Colored Joints.** To augment the appearance of the assembly and offer

some contrasting effect, colored dyes may be added to the solvent cementing agent. This effect has proven quite popular in the cementing of transparent stocks of materials. While the glue line is accentuated it can be accomplished in an artistic and attractive manner. The proportion of dye present is generally so small as to leave the strength and quality of the assembly relatively unaffected. Practically all of the solvent cements listed in the previous table can be had in a colorless form or liquid and are readily blended with the proper dye through dissolution.

Colored joints may sometimes identify the presence and spread of a colorless glue. The principle has applied not only to transparent plastics but also to opaque materials such as wood. A light green or red color for example, may not only identify a particular brand, but may also show whether or not adequate glue spread has been achieved.

**Evaporation Rate of Solvent.** The removal of the solvent from the glue line is essential to the development of strong, durable cemented assemblies among the thermoplastics. The solvent removal is accomplished in part by evaporation and in part by diffusion into the mass of the thermoplastic. The thermoplastics have strong affinities for the solvent cementing agents and will tend to hold and combine with the solvents. The rate of removal of the solvent is dependent upon its vapor pressure at room temperature, as some types will evaporate and dissipate much more readily. Generally the higher the molecular weight, the less readily will diffusion into the plastic take place, and at a slower rate. Besides, the higher molecular weight solvents generally tend to have higher boiling points and low vapor pressure. In cementing the thermoplastic to itself, the solvent cementing agent is usually applied to the joints already assembled, hence there is little opportunity for evaporation to take place, except at the outermost edges. If however, relatively large flat areas are to be joined, and an open assembly period is required before the parts are placed together, evaporation rate of the solvent must be carefully considered. More highly volatile solvents such as acetone and ethylene dichloride will evaporate rapidly if only lightly brushed on the surface. There must be liberal application of the solvent to wet the surface thoroughly and soften the material present. Under these circumstances it may be feasible to form a dope or lacquer of the solvent and have the thermoplastic cemented beforehand.

Solvents plus thermoplastics will possess much higher viscosity than pure solvent alone, and will in depositing a thicker film, retain the solvent at the glue line for a longer period of time. Various plasticizers may also be included in such formulations. Combinations of this nature are especially effective for paper and leather products and will be covered more fully in a later chapter. There is always the problem, however, of "skin-

ning" on the surface of such combinations, inasmuch as this skin may likewise prevent the attainment of optimum bonding qualities. "Skinning" tendencies may be substantially reduced through proper solvent combinations and the balancing of high boiling point solvents with low boiling point solvents. All slow evaporating solvents would be obviously unsatisfactory, as slow removal from the glue line will mean low strength for a long period of time.

**Toxicity.** In the handling of solvents for adhesives the same precautions should be exercised as in the application and spraying of lacquers and varnishes. This is rather important when large productions are involved, as there may be a considerable quantity of solvent vapor. This may not only constitute an explosive hazard, but may also represent a health hazard. Good ventilation should be provided. Chlorinated solvents, as well as benzene and toluene, are indicated for some of the thermoplastics earlier in the chapter. These cannot be handled promiscuously, as they will prove injurious to the health. All bottles should be labeled with adequate precautions for the consumer.

**Highly Plasticized Thermoplastics.** A few special notes should be made about the cementing of highly plasticized thermoplastics to one another through solvent cementing agents. While the high polymer content may show a particular affinity for the solvent cement, the plasticizer may or may not tolerate the solvent. More usually there is chemical compatibility between all components. However, the solvent may possess a better affinity for the plasticizer than for the high polymer. Under these circumstances, the plasticizer may tend to concentrate at the glue line in the presence of the solvent, leading to some unbalance and a weakening effect due to the presence of an excessive amount of plasticizer.

More difficulty is encountered in the cementing of highly plasticized thermoplastics than the rigid type of plastic material. This may be due not only to chemical reasons but also to mechanical reasons. If the materials possess considerable extensibility, as the glue line is stressed, differences in the extensibility of the glue line film and the body of the plastic may result in overstressing the glue. However, for the non-rigid, more rubber-like materials, good bonds may be obtained by special processes involving heat welding.

There may be components other than plasticizers which will interfere with the development of good bond strength. Various waxes or lubricants present in the formulation may bleed through to the glue line and result in an unsatisfactory bond. Solvents are not always necessary to bring about this condition, as it may occur spontaneously due to the proportion of chemical components in the material.

**Slush Molding by Solvent Welding.** The art of slush molding by

solvent welding offers a technique of binding together thermoplastic granules. By following principles and practices indicated in the preceding paragraphs it is possible to take some very fine granules of thermoplastics and weld them together with a mold to form a thin walled article. In practice the granules are not dissolved completely; they are only wetted on the surface and adhere firmly to one another as the excess solvent is evaporated. Thus the granules may be blown in by air and simultaneously wetted with solvent or else they may be introduced into the mold by hand, and wetted with solvent applied from a medicine dropper, and complete articles built up as in Figure 64. Very fine granules should be employed



Figure 64. Small articles of thermoplastics prepared by solvent welding of granules.

for fine grain texture. The surface may be built up to any desired thickness depending upon the amount of granules and solvent employed. Only a small amount should be added at any one time, to avoid too liberal an application of solvent, and the surfaces slowly built up with short periods of waiting between each application of material. When placed in a vulcanized rubber mold, or specially coated plaster of Paris, the solvent-wetted granules will capture the mold details quite effectively. Fine acrylic polymer and ethylene dichloride are one typical combination.

By producing complete dissolution of the granules and employing heat and pressure, the polymethyl methacrylate polymer and monomer are welded into dental plates and the like. This is an art widely established

by various dentists throughout the country. Many fine details can be captured from the mold impression, and the light color of acrylic permits dyeing with colors to simulate the inside of the mouth and the gum.

Granules of thermoplastics may also be wetted with solvents and applied to the surfaces of sheets stocks to achieve special decorative effects. These unusual combinations are made possible by the low viscosity solvent cementing agents and the ease with which most of the thermoplastics are dissolved. In applying solvents to the cementing of thermoplastic granules, excessive use of solvent may cause the outermost granules to fully dissolve and bridge across one another, erecting a barrier which may hinder further solvent penetration. In consequence non-uniform welding may be achieved.

**Pressure and Heat Requirements.** Most solvent cementing of thermoplastics is accomplished at room temperature and in the absence of much pressure. Heat will of course aid the dissipation of higher boiling point or lower vapor pressure solvents, though this is seldom required. When necessary, as may be in the case of bonding polyvinyl chloride-acetate, heat applications should be localized, to avoid insofar as possible distorting the balance of the article. On the other hand, as the articles become larger in size, pressure requirements necessitate a greater share of attention. The attachment of reinforcing ribs to the inside of transparent plastic bomber noses; the assembly of thermoplastic injection molded antenna masts; the manufacture of thermoplastic furniture, etc., necessitate assembly jigs to keep the parts in perfect alignment during the setting of the solvent adhesive. The design and the application of pressure from these jigs should follow good mechanical principles and avoid the development of localized stresses which may warp or deform the parts being cemented. Better pressure distribution can often be realized through sponge rubber pads or expandable tubes.

As pointed out earlier, the unit pressure requirements are entirely dependent upon the fit of the sections being assembled. A typical cementing jig for polymethyl methacrylate was described by Preston, who used a wedge-shaped punch to apply lateral pressure over the contoured surface<sup>1</sup>. For smaller assembly operations various pinch clamps are effective for holding parts together while the solvent cement develops the best strength in the joint. These pinch clamps are generally loaded by torsion springs or compression springs and usually develop pressures of 20 to 100 p.s.i. per clamp. Reinforcing ribs or additional strips are cemented in place with their assistance. While considerable hand labor is involved in taking them off and placing them upon the assembly the expense is generally less than a complete contoured form block which may apply cementing pressure. The thermoplastics generally soften sufficiently to leave some

mark or depression as evidence of the pressure of the clamp. The edges are generally concealed however, or machined to eliminate these defects.

**Defects in Joining Thermoplastics.** There are various defects which arise in uniting thermoplastics with the aid of solvent cementing agents. These defects and some of their remedies are outlined below.

*Small bubbles.* Small bubbles may be due to a number of causes including: entrapment of air; evaporation of volatiles usually during the time the glue line is setting; moisture or incompatible agents; and voids due to shrinking. The latter may resemble bubble or bare spots, though they are generally larger in area than the others. To eliminate the bubbles it is important to have sufficient cementing agent and dissolved polymer to fill all voids which may be created. If large, flat sheets are being placed together, the assembly should be wedge-fashion, so that as the two sheets are brought together by pivoting on one edge, the rolling bank of cement which is established will eliminate all possibilities of air (see

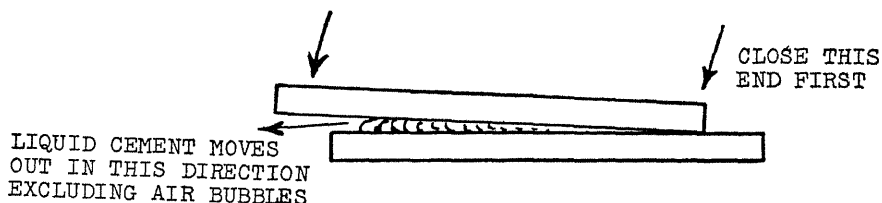


Figure 65. Eliminating air bubbles by wedge action.

Figure 65). This is important as air bubbles are probably the most frequent cause of this type of defect.

Uneven distribution of the cementing agent may result in some portions of the surfaces being low in cementing agents. If of a volatile nature, this may leave in the final assembly a bare spot low in strength. However; there is usually sufficient solvent cementing agent in the balance of the glue area to compensate for that lost from a small portion. Some solvent can usually be applied from a hypodermic needle to the void to clear up the joint.

*Dull, uneven appearance to the glue line.* This defect is more usually observed in transparent bodies and may be brought about by shifting of the parts being cemented after the cementing agent has taken its initial set. The strength suffers quite appreciably when this occurs and it is generally better to open up the assembly and reapply additional solvent cement. When sufficient strength has been developed, however, parts should hold firmly.

*Dirt and impurities.* The presence of dirt and impurities can be avoided if sufficient care is taken to perform cementing operations away from

dust-laden atmospheres and to insure clean tools and equipments for applying the solvent cementing agents. After the surfaces have been wetted they should be protected during their short open assembly period to avoid the settling of dust or other impurities. Of course the surfaces to be glued must be thoroughly cleaned beforehand.

*Crazing patterns.* Crazing patterns consisting of a cobweb of fine lines may be due to internal stresses in the material being bonded or highly localized stresses resulting from machining or from clamping pressures. Insufficient cementing agent also increases the tendency for craze patterns to form. Another contributing factor may be the sudden relief of clamping pressure. A clear, well cemented joint may craze if pressure is relieved too suddenly. On the other hand, it may take some service usage to develop stresses causing craze patterns on the glue line. To minimize their formation the areas being bonded should be as stress-free as possible, or the stress distributed over as large an area as possible.

*Blemishes immediately outside glue line.* Blemishes immediately outside of the glue line may be caused by excess cement squeezing out and depositing on or across the face of the thermoplastic material. Masking tapes unaffected by the solvent cementing agent generally provide an answer to this problem, as the excess will deposit on the tape, which can be stripped off and thrown away later. The writer has also found that a thin film of methyl cellulose or polyvinyl alcohol, applied from a water solution, will be quite resistant to organic solvents and eliminate the depositing of solvent cement in unwanted areas. Well fitted joints in which the solvent can be run by capillary action are seldom troubled with this type of defect.

### Heat Welding

One of the most effective methods of joining a thermoplastic material to itself is through the process of heat welding. Stronger and clearer assemblies can be made in this manner than by any solvent cementing agent. Its chief disadvantage is mechanical and the problems attendant upon applying highly localized heat to the glue line, followed by the subsequent application of pressure. The surfaces to be heat welded are brought to a very high temperature—generally at some point just above the decomposition point of the thermoplastic. This results in the formation of volatile matter of lower molecular weight and a molecular weight distribution conducive to good heat welding. While at this high temperature the surfaces are pressed firmly together.

The temperature at which thermoplastic materials may be heat welded are dependent upon a number of factors. Some materials require low temperature, while others require surface heats exceeding the decomposition range for the material. In fact, given a sufficient length of time some

materials may weld to themselves at room temperature on mere contact. The conditions for low temperature weldability appear to depend upon relative mobility of molecular groups in close proximity to the glue line, and plasticizers are an important influence. In examining those materials which possess good heat weldability, the following thermoplastics are recommended: Polyvinyl acetate, rubber hydrochloride, polyvinyl acetals, ethylcellulose (plasticized), and polyvinylidene chloride. Other thermoplastic rigid-type high polymers such as cellulose esters, polymethyl methacrylate, polystyrene, and polyvinyl chloride-acetate may also be heat welded, but at much higher temperatures. It is difficult in fact, to state a specific temperature at which heat weldability will occur, as this will be found to be a function of time, pressure, plasticizer content, and molecular weight of the material being bonded.

Among other phenomena which will influence heat weldability is the viscosity or flow characteristic of the materials versus temperature. Polyvinyl acetate grades for example, are softened quite appreciably in the temperature range of 200 to 300°F, depending upon the molecular weight. Parts may be heat welded with polyvinyl acetate at approximately 250 to 300°F. In fact, sheets of cellulose acetate coated with polyvinyl acetate possess good heat sealing properties at temperatures lower than possible with the cellulose acetate itself. Clear, transparent cellulose acetate sheets treated in this manner have been employed for the laminating of thin identification cards and photographs, a procedure which preserves these valuable papers for every day inspection.

Rubber hydrochloride ("Pliofilm") has an outstanding advantage in good heat sealability. This proved to be a very important factor in governing the selection and adaptation of this thermoplastic to the packaging of foodstuffs. Instead of the conventional method of applying some cement to the edges of the package about to be sealed, a heated knife or contact arm rapidly brings the material to welding temperature, closing the seams with heat. The heat must be carefully controlled in the case of thin foils; otherwise the foils may wrinkle and be damaged beyond repair. The rubber hydrochloride foil forms an excellent sealed joint which resists all attempts at opening, either mechanical or by moisture.

Regenerated cellulose is not readily heat sealed, unless it has applied to its surface some cellulose ester lacquer which will bond to an adjacent surface similarly coated. The cellulose acetate sheets do not readily heat weld until higher temperatures are reached. On the other hand, the better chemical compatibility of cellulose nitrate makes it probable that this cellulose ester as well as the cellulose acetate butyrate will heat seal more readily. Ethylcellulose has good heat sealing properties, a point which has been useful in the application of ethylcellulose as an insulating

foil to electrical equipments. Through proper heat sealing it is possible to close off the electrical coils from contact with the outside atmosphere.

In the heat sealing of thicker sections of thermoplastics, the processes of applying heat are considerably different. Instead of a concentrated heat passing through the body of the material, as in the case of the thin packaging foils, heat is brought to bear only on the surface of the material. There are various ways of developing this heat. One method is to employ a heated stainless steel, polished member in contact with the two surfaces to be heat welded. The advantage of this metal contact member is that the temperature can be controlled, heat being applied to the metal. The writer has found that temperatures of 600 to 650°F work best for the acrylic plastics, and as soon as the plastic surfaces begin to sputter and

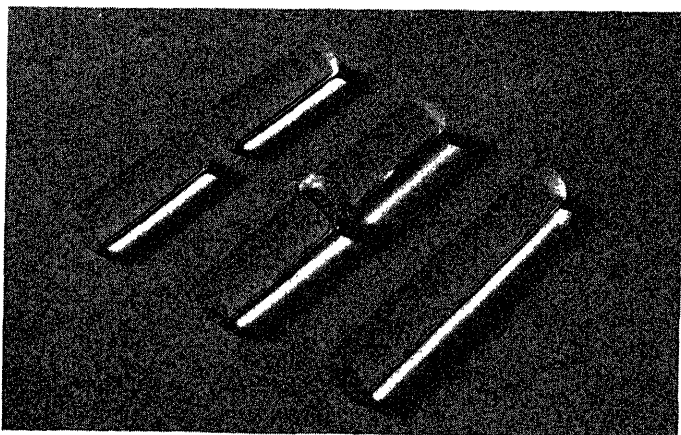


Figure 66. Acrylic rods at bottom have been heat welded—there is no visible evidence of weld line.

boil, the metal contact member is withdrawn and the parts placed firmly together. Two polymethyl methacrylate rods cemented together in this manner are illustrated in Figure 66<sup>20</sup>. There is no trace whatsoever of the glue line when viewed with the eye after excess has been removed. However, in polarized light the internal strains reveal where the heat welding took place.

The assembly of rods and tubes of extruded polyvinylidene chloride ("Saran"), popular in the field of chemical conduit, has found that heat welded assemblies give the best result. This is a rather fortunate coincidence for this polyvinyl resin, inasmuch as it is quite resistant to most solvents and the use of a solvent cementing agent is practically impossible. To assemble the tubes and rods in their proper relationship, it is necessary to have them properly assembled in a jig which when pressure is brought

to bear, will develop full and uniform contact pressure in the correct direction. Excess materials which squeeze out in assemblies of this nature must be cut or sanded off, and the joint can be polished if desired. When properly done there should be no visible trace of the glue line.

Instead of heating the thermoplastic in contact with a hot metal other alternatives are available. Hot air may of course be used, and the surfaces should be heated to the melting point and firmly pressed together to form a strong reliable bond. This technique has been employed upon polyvinyl resins<sup>3</sup>. A stream of hot gas may be directed against the thermoplastics to be joined by heat welding until a bead of molten material is formed; then the hot gas is moved forward at a controlled rate, providing for progressive heat welding of the material<sup>4</sup>. Reinhardt suggested a thermoplastic welding rod and a jet of hot gas inert to the plastic for heat welding the materials<sup>5</sup>.

Even more satisfactory than the methods described in the preceding paragraph are the methods of high frequency welding. Zade described two chief processes—continuous and discontinuous, the latter representing a spot gluing application. At a frequency of 50 megacycles, polyvinyl chloride sheets (0.005 to 0.030 inch) have been welded at a speed of 12 to 72 inches per minute<sup>6</sup>. To aid the high frequency generation of heat in the thermoplastic material, high dielectric constant fillers such as titanium dioxide have been suggested for polyvinyl acetals, polystyrene, polyacrylates, and cellulose derivatives<sup>7</sup>. The first evidence of high frequency heating of thermoplastics cements was by Pitnam, who applied the process to the cementing of shoe parts<sup>8</sup>. High frequency methods are well suited to generating heat throughout the entire thickness of the thermoplastic.

It is quite probable that the art of heat welding will play a more prominent rôle in the cementing of thermoplastics structures. Physical tests upon properly made joints indicate strengths about 90 per cent of the original material. It is to be recommended wherever it may be applied, though when curved and contoured surfaces are involved, greater expense in tooling is necessary to concentrate the heat where it will do the most good.

Heat in combination with plasticizers or solvents may be most effective. For example, if it is desired to weld an acrylic rod in the center of a flat sheet, the end of the rod may be brought to decomposition temperature in a hot flame and immediately placed upon the flat sheet which may have been previously wetted with acrylic monomer. Good welding will result.

The injection molding grades of thermoplastics possess good heat welding qualities. Not only may the molded articles be cemented in this manner, but the granules themselves will fuse to one another if heated in an oven at 350 to 400°F. The fusion may be quite complete, the granules sub-

stantially melting together on their surface. This is aided partly by the plasticizers in some of the materials. Results however are much more rapid and effective when conducted under the usual molding procedures of heat and pressure.

### Friction Welding

Another form of heat sealing, called friction welding, is of more recent origin<sup>24</sup>. Thermoplastics are welded to one another and to dissimilar materials by means of frictional heating. The two parts are rubbed together until quite hot and pressed firmly together while cooling. Good, clear and very strong bonds are obtained. In one simple application of this technique, a thermoplastic rod (or knob to be fastened to another assembly) is attached to the chuck of a slowly rotating drill press. The rotating piece is brought into light contact with the surface to which it will bond. In a few seconds the frictional heat will cause a slight smoking due to volatiles which form because of the heat, and a small amount of material will exude out from under the rotating part. The motor is stopped, and the parts pressed firmly together and held. A clean bubble-free joint will be prepared. Nylon, acrylics, casein, and others have been bonded in this manner. Preliminary cleaning of the surface is not necessary.

### Cementing of Dissimilar Thermoplastics

The cementing of dissimilar thermoplastics entails entirely different problems than the cementing of materials of the same chemical nature. For example, acetone, a good solvent for cellulose acetate and cellulose acetate-butyrate, if applied as a solvent cementing agent in an effort to bond these two dissimilar materials together, would produce relatively poor results. The very minimum requirements would, of course, be good chemical compatibility between the polymers and their plasticizers. Only then, in the presence of a mutual solvent some compatibility and good bonding may be effected. When joining two dissimilar thermoplastics which are chemically compatible it is usually more satisfactory to prepare a solution of both polymers and spread it on the surfaces to be joined.

The effects exhibited between two dissimilar thermoplastics may be unusual, as evidenced by blocking phenomena when these materials contact one another. Blocking represents the adhesion between two dissimilar thermoplastics, and is measured by the force required to peel the sheets apart. This may take place over a period of days or weeks and may occur between sheets of two dissimilar materials or the same thermoplastic with different proportions of plasticizer. It is particularly exhibited by highly

plasticized thermoplastics, as for example non-rigid polyvinyl chloride or polyvinyl chloride-acetate resins in contact with other polymers, and is marked by a migration of plasticizer from the material of high concentration to the material of low plasticizer concentration. As a practical method of providing union between two thermoplastics it does not have promise, though the phenomena involved yield data of theoretical significance.

High values of glue line shear strength may be obtained when solvent welding a thermoplastic to itself—of the order of 2000 to 3000 psi. Lower values will suffice for cementing thin sheets and foils. Consequently many tacky adhesives prepared from rubber derivatives may serve the purpose of uniting thermoplastics quite adequately. General purpose adhesives such as "Pliobond" and "Vulcalock" serve very satisfactorily for thin foils of widely dissimilar materials. Polyvinyl acetate, polyvinyl butyral, and polyisobutylene adhesives may also be employed in some circumstances. However, for heavier sections of thermoplastics, failures will occur in the glue line rather than the thermoplastic.

With respect to the heat welding of dissimilar thermoplastics, it is again a question of chemical compatibility. Certainly if the two materials may be hot blended together in all proportions they should be amenable to hot welding operations. Data on this combination are meagre and more work will have to be accomplished before more definite conclusions can be drawn.

### **Cementing of Thermosetting Plastics**

The cementing of thermosetting plastics may be readily accomplished with a number of thermosetting adhesives. The possibility of chemical compatibility and combination is very much less for fully polymerized thermosetting structures, than for the more soluble thermoplastics, though the results attained can be quite as high, if not higher. Among the thermosetting plastics which are considered in this section are molded, laminated, and cast sections of phenol or cresol formaldehyde, urea formaldehyde, melamine formaldehyde, phenolic and urea resin impregnated, compressed woods, and polyester resins. Among the thermosetting adhesives which can be considered are phenol and resorcinol formaldehyde; urea and melamine formaldehyde; polyester resins; and furfuryl alcohol polymers. The preparation of the adhesive agent, its application, and the curing conditions are considerably different from the procedures followed for thermoplastics.

There is no one single adhesive superior to all other types in applications to thermosetting plastics, and it is necessary to review the relative merits of each type before selecting the best material. In the following table

some empirical observations are made upon the behavior of each type of thermosetting adhesive:

Evaluation of Thermosetting Adhesives

Material Bonded	Acceptable Adhesives
Molded phenolic to phenolic	Cold setting furane, resorcinol, and phenolic adhesives
Cast phenolic to cast phenolic	Furane and resorcinol adhesives
Laminated phenolic to laminated phenolic	Furane and resorcinol adhesives
Molded and laminated ureas to molded and laminated ureas	Urea, furane and melamine types
Polyesters resins to polyester resins	Liquid polyester monomers and furanes

Setting characteristics of the various types of adhesives are listed in the accompanying table, which approximates pot life, pH, open assembly time, and curing conditions.

Characteristics of the Typical Thermosetting Adhesives

Adhesive Material	Volatiles (%)	pH of Glue Line	Pot Life of Glue (hrs.)	Open Assembly Time (min.)	Curing Conditions
Phenolic	40	1.0-1.5	2-3	5-20	Room
Furane	0	2.5-3.0	6-8	5-30	Room
Resorcinol	30	7.0-7.2	2-3	5-20	Room
Urea	45	2.5	2-3	5-15	Room
Polyester monomer	0	7.0	several days	short	heat to 300°F

Most of the thermosetting adhesives indicated in the table above are room or temperature setting. There are hot setting types which have been specifically developed for the bonding of woods which may also be considered in the bonding and fabricating of thermosetting structures. However, the room setting types are generally employed and when hot setting is required, the heat is applied to the glue line greatly shortening the time of cure to full strength.

There has been very little published work on the comparative strengths developed by the various thermosetting adhesives in the bonding of thermosetting materials. Most of the information has been related to the tests upon wood products, though a few results are available from the Forest Products Laboratory on the cementing of laminated high strength paper ("Papreg") and phenolic resin impregnated wood ("Compreg"). Some of the characteristics observed were the effects of pretreatments applied to the surface before gluing<sup>9</sup>. Chemical treatment with acid and

alkalies were found to improve the gluing characteristics with certain glues, though sanding proved to be the most generally satisfactory pretreatment. Pressures as low as  $1\frac{1}{2}$  psi were acceptable in bonding the laminated phenolic paper when the panels lay flat. The amount of failure in the laminate was over 90 per cent. Phenolic resin films were also employed with some degree of success, the results not being dependent upon moisture to an appreciable extent. Typical results from the report by Eickner are shown in the following table.

Glue	Surface Treatment	Dry Shear Strength-average* (psi)
Urea formaldehyde—hot setting, acid catalyst	None	0
	Wash with benzene	72
	5 minutes in conc. NaOH	174
	5 minutes in conc. H <sub>2</sub> SO <sub>4</sub>	581
	Sanded	584
Phenol-formaldehyde—hot setting, alkaline catalyst	None	574
	Benzene	556
	5 minutes in conc. NaOH	577
	5 minutes in conc. H <sub>2</sub> SO <sub>4</sub>	249
	Sanded	534
Urea formaldehyde—cold setting, acid catalyst	None	0
	Benzene	0
	5 minutes in conc. NaOH	117
	5 minutes in conc. H <sub>2</sub> SO <sub>4</sub>	330
	Sanded	612

\* Strip shear test method on three-ply panels (see Chapter 20 on test methods)

Good results were also reported for glue spreads from 25 to 75 pounds per thousand square feet and for bonding pressures up to 250 psi. This would indicate the availability of a number of satisfactory adhesives for laminated phenolic panels which were sanded. In tests upon phenolic resin impregnated wood Eickner found several good thermoplastic resins, though these were deemed unsatisfactory for aircraft use<sup>10</sup>. The resin impregnated wood employed in these tests were made from 1/16 inch birch veneers impregnated to a resin content of 30 per cent. Sanding of the finished "Compreg" surface was found to be a condition best suited to subsequent gluing operations. Solvent washing or acid and alkali pretreatments were not found to improve the results and were generally considered unsatisfactory. Some inconsistencies were reported for the low temperature setting urea formaldehyde and phenol formaldehyde types, though this was attributed to rough surfaces on the "Compreg". Typical results ob-

observed in bonding of the phenolic resin impregnated and compressed wood are abstracted from reference<sup>10</sup>, with results for furane resins included in addition to these. Tests were conducted in the same manner in all cases:

Strip Shear Tests Upon Compreg Panels

Glue	Curing Conditions	Average Dry Shear Strength (psi)
Polyvinyl acetate	140°F—cool under pressure	800
Polyvinyl formal	19-24 hours' assembly, 140°F, cool	762
Hot Setting phenolics (several)	25 mins. at 315°F	550-750
Melamine-formaldehyde	140°F	725
Furane adhesive—acid	room	800
Phenolics-acid	room	600-700
Phenolics-alkaline	room	550-600
Urea formaldehyde-acid	room	650-800

When the tests result in failure in the laminated material, it is difficult to make a comparison between the glues, because of the low shear strength of the materials being tested. Then the actual values of shear strength are entirely a function of the test condition and the nature of the test samples. However the results are of qualitative value. In the strip shear type of test, both tension and shear forces are present—to what extent depends on the test piece. Thus in the above table, when shear strengths are above 750 psi there is 100 per cent failure in the "Compreg", which means that all the glues giving satisfactory results at shear strengths above approximately 750 psi may be considered acceptable for bonding this particular material. However, the above table does not give data showing the best of these adhesives.

While the above results have been performed upon "Papreg" and "Compreg", they may be indicative of the probable behavior of thermosetting adhesives with other types of materials. No extensive report has yet been made on shear strength behavior on various types of molded phenolics, urea, or melamines and only a few brief results are available. It is to be expected that most of the thermosetting adhesives will show a good performance in contact with cold and hot water, as they not only possess a good inherent degree of resistance, but also the non-porous structure of the materials they are bonding should minimize the effects of contact with water.

Considerably better results have been reported in bonding laminated phenolics to laminated phenolics when the surfaces are not sanded—about double the shear strength than obtained with any other adhesive<sup>11</sup>. These results were obtained with furane resin adhesives. A three block shear sample is employed, such that substantially pure shear is developed.

The results indicate a shear strength in excess of 4500 psi for this cold setting adhesive. Even after one week of boiling in water or 6 months at a temperature of 200°F, the adhesive bond is still as good as the original. On the other hand, when the surfaces are sanded, the shear strengths are of the order of 2500 to 3000 psi. The fact that failure occurs completely in the laminated phenolic canvas when unsanded surfaces are employed is indicative that shear strengths may be higher, and in tests upon cast

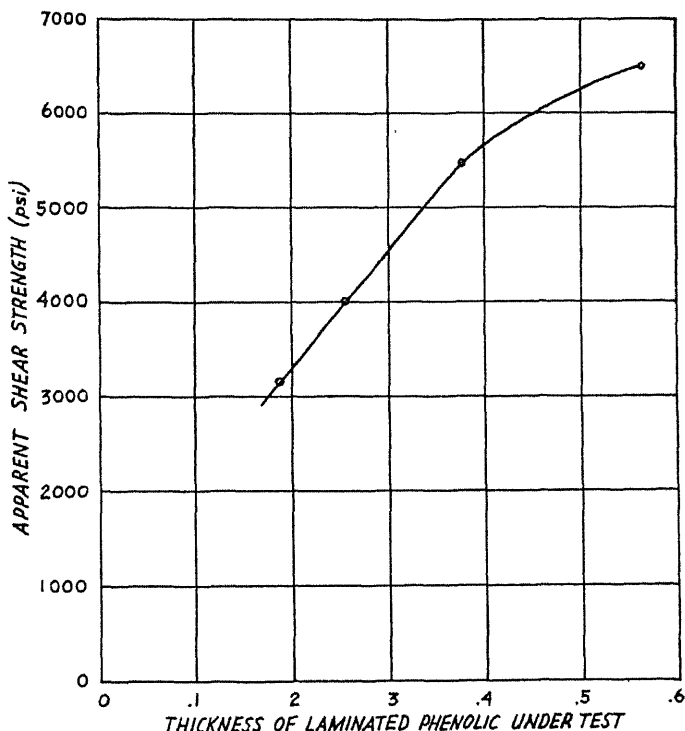


Figure 67. Apparent shear strength of laminated phenolics, canvas base, cemented with furane "Resin X-2" adhesive.

furane resin glue films shear strengths of 6500 p.s.i. were obtained. In another series of tests on the application of furane resin adhesives (Resin-X-2) to the bonding of laminated phenolic, canvas base, a relationship was established between the thickness of the laminated stock and the apparent shear strength. Unusually high shear strengths are reported in Figure 67, for the thicker laminates<sup>25</sup>. In the same paper data are given on bonding of all makes of commercial phenolic laminates with furane adhesives.

As new and improved types of thermosetting adhesives are developed for

bonding thermosetting plastics it becomes apparent that the limiting factors will not be in the adhesive but in the material to be bonded. From the writer's own observations the limiting pure shear strengths of various thermosetting laminated plastics are as follows (tested upon 4 inch panels): These tests were observed in cementing tests where the shear ran parallel to plane of the laminations.

Laminated phenolic—canvas base—4500 psi

Laminated phenolic—paper base—1500 psi

Masonite die stock—lignin—1000 psi

Various low pressure polyester resins—1000–2500 psi

There appears to be a considerable difference in the results of bonding low and high pressure laminated materials. This may be observed for some of the polyester resins; at the time of glue failure the resin may pull away from the glass fiber base or lamina which it ostensibly bonds. On the other hand, a diagonal failure through the test piece can be repeatedly obtained with high pressure laminated phenolics. Only when a true bond is produced such that the shear test produces a failure through the material—rather than picking fibers or chunks off the surface—can it be said that the ideal in bonding conditions has been obtained, for then the cemented assembly acts as an integral unit.

Developments in polyester resins in the low pressure laminating field are growing and it is likely that greater share of attention will be given to the problem of bonding these materials. In some instances, the same polyester resin used for laminating may be employed for gluing purposes, though the air in the atmosphere may influence the results to some extent and prevent the proper setting of the polyester under heat. For assembly work however, low temperature setting thermosetting adhesives will probably prove the most practical. Inasmuch as these materials are more resistant to pH variations than the wood or cellulosic products, very high and very low pH should not exhibit any pronounced effect.

The percentage resin in the outermost surface will influence the bonding results to an appreciable extent if smooth surfaces are to be preferred for the bonding operation. This has been observed by the writer in bonding phenolics with furane resin adhesives, which give higher shear strengths when the top surface layers have resin contents of 35 to 40 per cent, than when the resin contents of the top layers are 55 to 60 per cent. Our knowledge and understanding of the bonding of materials is meagre when we come to the organic plastics. Much fundamental work remains to be done—answering such questions as: the effect of moisture content on unsanded surfaces; the optimum resin content on the surface; the effect of different amounts of resin on the bonding; the influence of pH; the question of sanded

versus unsanded; etc. It is the writer's opinion that when the optimum results are obtained, it will be upon an unsanded surface where true specific adhesion can be manifested.

### Miscellaneous Assemblies of Organic Plastics

There are several interesting combinations of miscellaneous organic plastics which do not fit into any of the categories previously examined. Some of these are reviewed in the following paragraphs, and emphasis placed upon the bonding problems involved. In the application of partially polymerized thermosetting resins to fabrics there is always the tendency for the resin to penetrate excessively and embrittle the fabric. Beck solved this problem through application of a thermoplastic resin to the fabric base before the thermosetting adhesive was applied<sup>12</sup>.

Wood veneers are assembled to plastic sheets through various types of adhesives. Moss described a composite laminate in which wood veneers of lesser thickness than the plastic sheet, were cemented to cellulose acetate to form a decorative assembly<sup>13</sup>. Some manufacturers are bonding a thin layer of cellulose acetate sheet to a thicker core of plywood. The resulting plastic facing can be quite attractive in appearance, especially when it is stiffened by a low cost base. The cementing problem for the thin acetate sheet is not easily solved, as solvent type cements tend to wrinkle the surface unless maintained under pressure. A tacky polyvinyl acetate composition may offer certain advantages over a pure solvent or solvent combination. A composite floor panel designed to withstand 800 pounds per square foot has been made by one Mid-western concern. The core is spruce wood made up of narrow strips with surfaces of veneer which may be faced with vulcanized fiber. Vulcanized fiber faced plywood has proven useful for aircraft assemblies, the combination being made possible with thermosetting adhesives<sup>14</sup>.

Hot press laminated wood veneers to which is bonded a loosely matted fibrous sheet with thermosetting resin diffused throughout prepares a hard surface which masks the wood grain<sup>15</sup>. Laminated plastics with combinations of cellulosic layers and glass cloth layers are quite common. Ripper describes one in which the bonding medium is an amino plastic resin adhesive<sup>16</sup>.

Special safety glasses have invited unusual bonding and assembly problems. One interesting assembly provides for extension of the flexible inter-layer beyond the edges of the glass faces<sup>17</sup>. This flexible layer can be used as a leakproof gasket. Special adhesive problems are entailed when assemblies are made of polyvinyl butyral sheet to polymethyl methacrylate<sup>18</sup>. Attractive combinations have been prepared of opaque thermosetting phenolics and transparent acrylics with the aid of furane resin adhesives.

These composites have done much to extend the decorative appeal of both materials and when colored sheets are combined with the transparents, the effects are quite attractive<sup>19</sup>. Figure 68 illustrates a typical effect achieved through such combinations.

The development of "Polaroid" glasses have necessitated the preparation of shatter-proof laminates of cellulose acetate. Polyvinyl acetate plasticized with glycerol triricinoleate has been used as the adhesive<sup>20</sup>. Nitrocellulose has been laminated to a sheet of polyvinyl alcohol by means of an adhesive prepared from a mixture of the two components dissolved in 25 per cent of methyl cellosolve, 12 per cent of H<sub>2</sub>O and the balance methanol<sup>21</sup>. The grade of polyvinyl alcohol employed had 65 to 85 per cent of OH groups, the remainder being polyvinyl acetate<sup>21</sup>. A shatterproof lam-



Figure 68. Phenolic-acrylic laminates prepared with furane adhesives.

inar structure has been prepared from polymethyl methacrylate and a nitrocellulose coated surface of cellulose ether. The bonding agent was prepared from liquid monomers and copolymers of acrylic and methacrylic esters<sup>22</sup>. Vinyl and vinylidene polymers are united with methyl methacrylate monomer containing benzoin, in ultraviolet light<sup>23</sup>.

The welding of thermosetting phenolics to themselves is not always accomplished chemically if the material is in an advanced state of cure. In some tests the writer observed the weldability of a phenolic molding compound to itself, after one portion had been partially cured in the mold for different intervals of time. The second portion of the molding compound was added directly to the first portion, after the latter had been partially cured. The weld strength was determined by sanding a flat edge and delaminating the samples with a steel ball at the position where both halves of the molding compound joined. Results were as follows:

## Molded Parts Cured at 320°F

Cure of First Half ( <i>minutes</i> )	Cure of Second Half ( <i>minutes</i> )	Delamination Load in Pounds
1	10	775
1½	10	640
2	10	350

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## Chapter 17

### Adhesives for Metal and Rubber

The subject of adhesives for metal and rubber is best presented in the same chapter inasmuch as many of the important metal adhesives are prepared from a rubber base. In recent years there has been a growing interest in the bonding of metals as an assembly operation, especially when the metal is to be united to another material, usually a non-metal. When metal to metal assemblies are required, welding, rivetting, brazing, and soldering operations have been and will continue to be widely used techniques. On the other hand, where because of the delicate nature of the parts in question it becomes impractical to apply the high temperatures of metal welding operations, the assembly of such materials with plastics and rubber adhesives may become feasible. Temperatures as high as 350°F may be needed for setting some of the plastics or rubber adhesives, but seldom higher; this is certainly much less than the temperature required for metal welding. Besides, these adhesives permit the attachment of dissimilar materials.

For assembly operations at room or low temperatures, rivets, bolts, screws, etc., are common methods of attachment as they are the most economical and practical means of fastening metal parts together. The low temperature setting adhesives on the other hand are not assembled and cured as rapidly, but the advantage they have is the distribution of stress through the cemented region over a wide area instead of at a single point of attachment as in the case of a rivet or screw. The assembly of metal components may be more practical with high polymer adhesives than by means of mechanical attachment, as for example, in the construction and assembly of integral airplane fuel tanks in the wing structure. Only films of high polymers will give proper sealing to prevent loss of gasoline; the structure is too complicated for ordinary metal seam welding, and not leakproof with rivet attachments.

For many of the sheet metal to metal assemblies, rubber base adhesives are used because they are resilient enough to avoid development of high stress concentrations as the metal panels are vibrated or flexed. As will be seen from the discussion in this chapter it is recommended that many metal to metal assemblies be completed with a layer of rubber sandwiched between the surfaces to be bonded. Bonding to rubber is generally

considered more feasible than bonding to metal surfaces, though where vulcanized rubber stocks are involved, the problem becomes more difficult. Most bonding to rubber takes place at the time the rubber is vulcanized. Even then the problem is not an easy one because the number of good rubber adhesives for producing bonds to rubber stocks is relatively few. The problem is rendered more difficult perhaps by the fact that today although there are many types of synthetic rubber an outstanding general adhesive for bonding is not available. The best materials for rubber bonding are the cyclized rubbers and chlorinated derivatives; by referring to Chapter 8 on rubber adhesives, the various modified types may be reviewed.

Summarizing, we find that metal to metal assemblies with high polymer adhesives are justified under the following conditions:

- (1) When the temperatures of conventional metal welding or brazing may adversely affect metal parts.
- (2) When areas to be bonded are not easily reached from the outside, necessitating prior application of adhesive before parts are placed together.
- (3) Where the shock, sound, and vibration absorption qualities of a rubber sandwich material prove beneficial.
- (4) When a temporary bonding action is required.
- (5) When at room or low temperatures metal parts must be joined in full contact at the glue line, without concentrating the assembly and subsequent stresses at a few points of attachment.
- (6) To eliminate rivet heads or screw heads, leaving smooth exterior.

In bonding metal to other materials, there is no question as to the efficacy of high polymer adhesives. Metal welding, brazing, or soldering operations are effective only upon certain metals and are not useful, for example, in joining wood or rubber to metals. Applications of wood- or rubber-faced metal sheet are growing and extending the role of metals in specialized functions. For example, there is no sealer against weather as effective as a continuous sheet of thin metal gauge cemented to the outside of a wood structure; the wood receives an impermeable moisture barrier. In this chapter considerable space will be devoted to the problems of producing composite laminates of metals to other substances.

The rubber bonding problem will be discussed concomitantly, because of the important role played by this material in rubber-metal assemblies. Bonding may be accomplished with a vulcanizable rubber stock or with a completely vulcanized rubber or synthetic rubber stock. Generally the rubber is the weaker of the members being assembled, and the criterion of a good bond is failure in the rubber when tested to destruction.

### Metal to Metal

The optimum in a metal to metal union is an assembly operation at room or low temperature which when tested to destruction results in a complete metal failure. There is no adhesive material produced as yet which possesses sufficient strength to exhibit this ideal condition, except in the case of very thin gauge metal sheets. Shear strengths on the order of 4000 psi have been obtained, though this value is very much less than the strength limitation of aluminum and steel. Processes of metal fabrication would be revised substantially if the optimum condition could be realized. It has only been during the past few years that appreciable gains have been made in the art of bonding metal. Water dispersed animal and vegetable adhesives have never proven satisfactory and hope was never entertained for bonding metals with high polymers until the advent of modern rubber and synthetic resin adhesives.

Interest in the possibilities of synthetic resin and rubber adhesives for the bonding of metals was awakened in this country by the development of "Cycleweld", which as pointed out in the Chapter 8, was a modified form of rubber product. Unusually high results were developed with this material, particularly in the bonding of sheet aluminum, where shear strengths on the order of 3000 psi (figured on basis of failing load divided by glue area) were obtained. For thinner grades of aluminum and aluminum alloy sheets, this load was considerably more than that developed when rivets were employed. For reference purposes, bearing strengths of aluminum alloy rivets and sheets, as reported in the ANC-5 bulletin<sup>1</sup>, are reproduced below:

Allowable Bearing Strength of 24 ST Aluminum Alloy (lbs)

Diameter of Rivet (in)	Sheet Thickness					
	$\frac{1}{16}$	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{3}{8}$	$\frac{1}{2}$	$\frac{3}{4}$
0.020	112	168				
0.025	140	210	281			
0.032	180	269	360	449		
0.040	225	337	450	562	675	
0.051	286	430	573	716	860	1147
0.064	360	539	720	899	1080	1440
0.072	405	607	810	1012	1215	1620
0.091	511	767	1023	1279	1535	2047
0.128	720	1079	1440	1799	2160	2880
$\frac{1}{8}$	1054	1581	2109	2635	3164	4218
$\frac{1}{4}$	1406	2108	2812	3514	4218	5625

The "Cycleweld" bonding process developed for woods, metals, and ceramics, found its way into many applications involving sheet aluminum

alloy. The advantages claimed were flush and stronger assemblies. While all the rivets and rivet heads were eliminated a few were maintained at strategic positions at the ends of the sheet. Cemented parts such as ailerons withstood vibration tests very well<sup>2</sup>. Under these tests metal failures rather than glue failures were experienced. Sub-assemblies such as wing flaps, stabilizers, heating ducts, bomber floors, etc., were manufactured. After the adhesive is brushed into place, parts are placed under heat and pressure for 10 to 15 minutes, at 200 to 300 psi, and about 325°F. The process is claimed to be quicker and less costly than spot welding of aluminum alloy sheets, and it was noted that some 30,000 metal parts were assembled in this manner<sup>3</sup>.

While interest in this metal bonding process was high early in 1942, late in 1943 attention was diverted to other metal bonding processes. Durability at temperature extremes and behavior in the presence of salt water offered further problems to be overcome. Considerable interest was displayed, however, in wood veneer-faced metal parts, prepared by hot setting metal adhesives, which permitted the employment of cold setting adhesives in the field. Field assemblies were effected with cold setting cements applied to the exposed wood veneer face.

The possibilities of developments in rubber base adhesives which preceded the "Cycleweld" process, were not realized until the latter attracted attention to industrial applications. This material, called "Reanite", claimed bond strengths in shear ranging from 1000 to 3000 psi. After application to the metal surface and thorough air drying, parts were pressed for 15 minutes at 290°F.<sup>4</sup> One of the early patents on this material described it as an intimate mixture of solid rubber, weak acids, and solid salts of strong acids<sup>5</sup>. The "Cycleweld" adhesive has only been described as a modified form of rubber and various patents appearing under the authorship of its inventor to date have indicated combinations of various rubbers with other resins. While "Reanite" appeared first under some Canadian patents by Reaney, its development was undertaken in the United States by the U. S. Stoneware Company. Chrysler Corporation sponsored the "Cycleweld" developments.

In addition to these metal bonding method, still another received attention from abroad. This was called the "Redux" process and involved a thermosetting adhesive base in conjunction with a thermoplastic vinyl resin. The process, developed by Aero Research, Ltd., in England, was adopted by Resinous Products and Chemical Company in this country. Bonds were obtained on steel and aluminum which exceeded rivetting strength<sup>6</sup>. The product has been the subject of much official testing in Britain in connection with aircraft assembly. Its use on Alclad sheet metal has been emphasized, though for bonding laminates, wood, "Com-

preg", and the like, it has shown much promise. The "Redux" process is based upon two components, a clear reddish-brown low viscosity solution (a phenolic resin) with a specific gravity of 1.1, and a white, "Redux" powder which is sprinkled over the surfaces wetted with the reddish liquid. Parts are pressed at a temperature of 300°F. In normal usage 7 pounds of powder are used per gallon of liquid. The liquid has poor storage characteristics, however. Most of the rubber adhesives for bonding metal, such as "Reanite" and "Cycleweld", will not store indefinitely at room temperature without gelling.

Tests results reported by the manufacturer of "Redux" adhesives report tensile shear strengths as high as 3500 to 4000 psi upon 0.064 inch Alclad aluminum alloy sheet, and 2500 to 3000 psi upon 0.040 inch sheet stock. The material, however, loses strength appreciably in the neighborhood of 200°F. It must be cooled under pressure to around this temperature before assembled parts can be taken out of the press. The bonding schedule for the "Redux" adhesive is as follows<sup>7</sup>:

Temperature °F	240	260	280	300
Time in Minutes	50	30	15	5

The glue spread for the "Redux" liquid should be 20 to 25 pounds of liquid for 1000 square feet. It is applied to each of the two surfaces to be bonded. Open assembly times of 5 minutes to several days are satisfactory. The method has also been used for attaching light alloys to wooden parts, providing for localized reinforcement at points of high stress concentration<sup>8</sup>.

Another important metal bonding adhesive was developed by Havens at Consolidated-Vultee Aircraft Corporation. This material was known as "Metlbond" and described as a synthetic resin-rubber adhesive. Shear strengths in excess of 3000 psi were obtained which were comparable to or greater than those required for spot welding. The rubber base cement gave good adhesion to the metal and flexibility to the bond, while the plastic base component flowed under pressure to fill inequalities of the material to be joined<sup>9</sup>. There were several variations of the "Metlbond" procedure in order to accommodate a variety of bonding conditions. These were described as follows: (1) synthetic rubber base cement which set under 100 psi at 330°F for 10 minutes; (2) an adhesive involving a synthetic rubber component and a plastic component which set under 15 psi at 330°F for 20 minutes; (3) a tape requiring 250°F curing temperature and 100 psi; and (4) a 1 psi, 300°F curing temperature adhesive. Further modifications included the application of "Metlbond" as a primer coating set by heat and followed in turn by a low temperature setting adhesive capable of bonding to the primer coating. An important applica-

tion which has been cited is the cementing of the leading edge of the wings of a "Liberator" bomber with the above adhesive<sup>10</sup>. Another effective assembly is the attachment of aluminum alloy to Fiberglass laminates. Applications to dies and tools are also known<sup>11</sup>. "Metlbond" and "Cycleweld" were approved by the U. S. Army for aircraft assemblies.

A new metal bonding cement by B. F. Goodrich Company, named "Plastilock 500", has demonstrated good bonding qualities for many materials. Temperatures required for bonding are 250 to 350°F and shear strengths of 3250 psi have been obtained in metal to metal assemblies<sup>12</sup>. Various others have been developed from time to time, and good results have been obtained in their application to the bonding of metal parts, though at present they appear to be limited to around 4000 psi shear strength. We will examine shortly the dependence of shear strength values upon the shape of test specimens and the test conditions. It would seem that the goal for the ideal metal adhesive still lies ahead. Most of the strong metal bonding types require high temperature for setting, and while this is not necessarily injurious to the metal, it means that considerable production must be involved to justify tooling costs of applying the correct heat and pressure for curing. For the most part unit pressures of 100 psi are not too excessive, though greater attention would undoubtedly be given to lower temperature room setting adhesives for metals. In the latter application, it is desirable to develop a good primer coating for the metal. This primer coating could be set by heat; when it became necessary to fabricate and assemble the metal part, low temperature setting adhesives could be used.

**Cementing of Motor Laminations.** In addition to the bonding of aluminum alloy sheets in aircraft fabrication processes, there has been a considerable amount of work accomplished in cementing together the thin laminations of silicon steel comprising electric motor construction. The shear strengths which are to be developed are considerably lower in this instance, and in most cases the assembly may be accomplished by some mechanical attachment such as long assembly screws. However, to reduce the chatter and hum of the laminations during operation and to insulate them from one another, a thin layer of adhesive or varnish is applied. Polyester resins and unsaturated alkyds have been used for cementing such metal laminations together<sup>13</sup>. Ford employed a polyvinyl resin for such purposes, comprised of 20 to 80 per cent of polyvinyl acetal, 0 to 80 per cent of polyvinyl acetate, and up to 20 per cent of phenol formaldehyde resin<sup>14</sup>.

The cementing of motor laminations is a somewhat specialized process; the problem of securing good adhesion to the steel is a pressing one, and not easily fulfilled by many resins. It will be noted that most of the

efforts have been directed towards the employment of a more flexible type of adhesive. This is entirely permissible as there is little or no shearing force tending to separate one lamination from the other. Plastic materials have also been employed in bonding motor winding and laminations into an integral structure by common dipping procedures, followed by baking. Because of their low cost and retention of flexibility, asphalt or bitumen base varnishes are widely employed for this purpose. More recently however, the synthetic thermosetting resins have been applied, culminating perhaps in the complete transfer molding of a phenolic plastic about a wound rotor as a core. The problems of thermal differences of expansion and contraction must of course be contended with.

**Cements for Iron Vessels.** Low in cost but of definite utility are various "iron cements" which have been known to steam fitters and pipe fitters for a number of years. Most common of these are glycerine-litharge compositions which applied to pipe threads afford good bonds and seals. These cements are unique in their ability to withstand the corrosive action of many solutions and reasonably high temperatures. They may further be used to fill depressions in porous castings. While in a shear test they would not exhibit unusually high values, their low volatile content and ease of application make them popular for general repair work. Various other iron cements employ either iron filings or powdered iron in combination with refractory materials such as clay, or perhaps plaster of Paris or sulfur. One well known composition ("Smooth-on" Iron Cement) employs 60 parts of precipitated iron powder, 2 parts of ammonium chloride, and 1 part of sulfur. These proprietary compositions are employed to fill up cracks in porous castings or as a general purpose cement for iron vessels. For filling the cracks of porous castings there are, however, more satisfactory low viscosity thermosetting resins. Slight air pressure applied to these castings can effect a good penetration and filling of the voids.

**Preparation of the Surface for Metal Bonding.** Too much emphasis cannot be placed upon the importance of adequately preparing the metal surface for subsequent bonding operations. All of the cements manufactured for bonding aluminum and steel necessitate thorough cleaning. The Army Air Force specifications recommend a detailed procedure for preparing and cleaning aluminum alloy and steel surfaces<sup>15</sup>. An outline of their procedure follows:

### *Aluminum Alloys*

Surfaces to be bonded shall be cleaned by washing the parts in a cleaning bath, rinsing in running water, followed by immersion in a chromic acid bath.

*Cleaning bath:* The parts are immersed for 3 to 5 minutes in a cleaning bath at a temperature of 160 to 185°F. The composition of the cleaning bath shall be as follows:

Anhydrous sodium metasilicate	3.6 ounces
Alkyl aryl sodium sulfonate	0.4 ounce
Tap water	1 gallon

Parts are thoroughly rinsed in running water and surfaces examined for discontinuity of water film indicating presence of grease or impurities.

*Chromic acid bath:* Parts are immersed in a chromic acid bath maintained at a temperature of 140 to 160°F for 1 to 3 minutes. The composition of the bath is as follows:

Chromic acid	45% by weight
Tap water	95%

Rinse in clear, cold running water and dry in air.

### *Steel*

Surfaces are prepared by immersion in a cleaning bath, rinsing in water, immersing in a pickling solution, and then in a bright dipping bath.

*Cleaning bath:* Parts are immersed in the following cleaning solution at its boiling point for 1 to 5 minutes:

Sodium carbonate	2.0 parts
Sodium hydroxide	2.0 parts
Rosin soap	0.5 part
Tap water	1.0 gallon
Alkyl aryl sodium sulfonate	0.5 ounce
Anhydrous sodium metasilicate	3.0 ounces

Parts are thoroughly rinsed with running water after removal from cleaning bath.

*Pickling bath:* The parts are immersed in a pickling solution at 60 to 70°F for a period of 2 to 4 minutes. The composition of the pickling solution follows:

Conc. $\text{H}_2\text{SO}_4$ —sp. gr. 1.85	10% volume
Conc. $\text{HNO}_3$ —sp. gr. 1.42	10% volume
Tap water	80% volume

After thorough rinsing in cold water, the parts are ready for the bright dipping bath which prepares the steel surface for the cementing agent:

*Bright dipping bath:* Parts are immersed in the bright dipping bath for  $\frac{1}{2}$  to 1 minute at 60 to 90°F. The composition is as follows:

Conc. HCl—sp. gr. 1.26	50-60 parts by volume
Hydrogen peroxide (30% sol.)	2    “    “    “
Tap water	38-48    “    “    “

Thorough water rinsing and drying follow the bright dipping bath.

The above procedures may appear to be long and somewhat involved for production, though the results warrant the efforts spent in this direction. The Army Air Force specifications indicate a minimum tensile shear strength of 2500 psi (single overlap of one-half inch). In lieu of the above, though offering much less satisfactory results, are the techniques of solvent cleaning and wiping. One British specification offers a treatment found to be very effective in preparing Alclad aluminum<sup>16</sup>. After thorough degreasing with carbon tetrachloride or acetone, immerse parts in the following acid bath for 20 minutes at 140 to 150°F:

	parts
Sodium dichromate	1
Conc. sulfuric acid	10
Water	30

Another alternative cleaning method is light abrasion of the surface with a fine steel wool saturated with solvent suited for degreasing. In any cementing of metal components for structural purposes, it is essential that a carefully planned cleaning and surface preparation schedule be followed.

**Influence of Physical Dimensions at Glue Line on Results.** Considerable work has been accomplished on the influence of physical dimensions and spacings upon the shear strength. Most of the metal adhesive specifications suggest glue line thicknesses of 2 to 4 mils, though this is naturally dependent upon how well the surfaces have been fitted together and how readily the adhesive flows when it is put under heat and pressure. Goland and Reissner have presented an excellent analysis of stresses in cemented lap joints<sup>17</sup>. They analyzed the stress distribution, particularly at the edges of the cemented joints, for relatively flexible and also inflexible cement layers, relating their results to the dimensional parameters of the overlapped joints. Dividing the cement stresses into pure shearing stress and a normal stress perpendicular to the glue line, they computed for inflexible adhesive layers that the stress concentrations are very severe nearest the edges. The normal stress may have as high a peak stress as 4.3 times the stress in the sheet at the start of loading and in close proximity to the edges, though this decreases to practically zero at a ratio of 0.4 for the distance from joint edge to sheet thickness. The shearing stresses may also attain a high peak value, as illustrated in the accompanying sketch taken from the paper of Goland and Reissner (Figure 69). The

stress concentrations are still high at the edges of the inflexible cement, though they grow less severe as the stress in the sheet metal develops. On the other hand, the stress concentrations are much less severe for flexible-cement layers. While the peak values of shear stress and normal

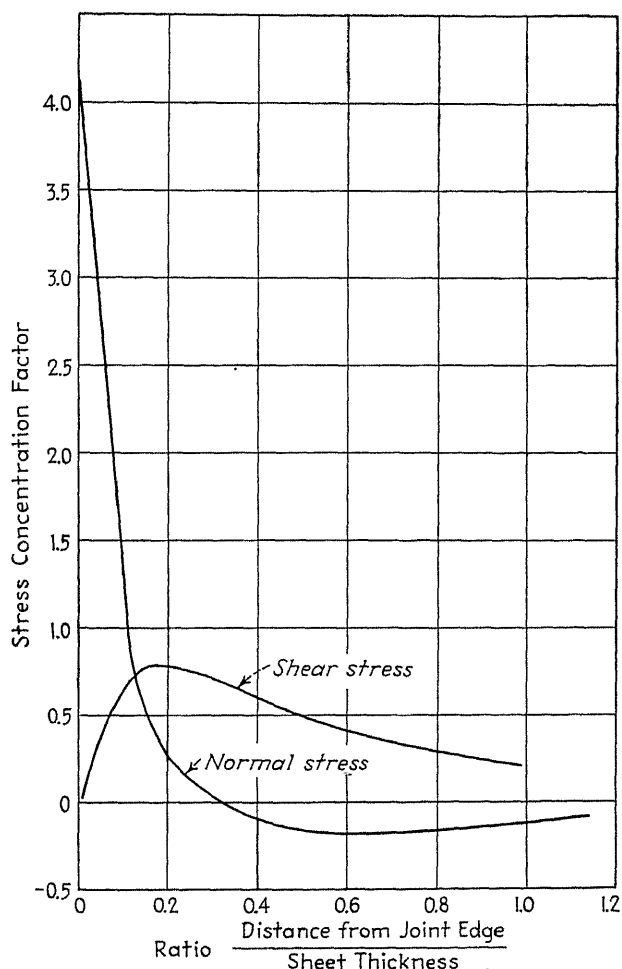


Figure 69. Results of Reissner and Golan for inflexible cements.

stress are still greatest at the edges, they are much less pronounced than for the inflexible layers, with both of these stresses about 0.12 of the stress in the plate. The shearing stresses are much more uniform along the length of the cemented region than the normal stresses, which change abruptly away from the glued edge.

It is almost imperative that good fillets be built up at the edges in the event that a relatively inflexible type of adhesive is employed in cementing metal panels together. The results of tension shear tests upon aluminum sheet indicate the prevalence of pronounced tension or normal stresses as well as shear stresses, by the appearance of the failed test piece. The amount of permanent bending in the sheet in the proximity of the glue line is quite pronounced. As may be expected, with thinner gauge sheets the apparent shear strength falls off quite markedly. This is owing to the fact that most of the rubber adhesives employed for bonding metal have a lower (about 1/2) tension or normal stress to metal surfaces than shear strength parallel to the glue line. When testing the tension shear

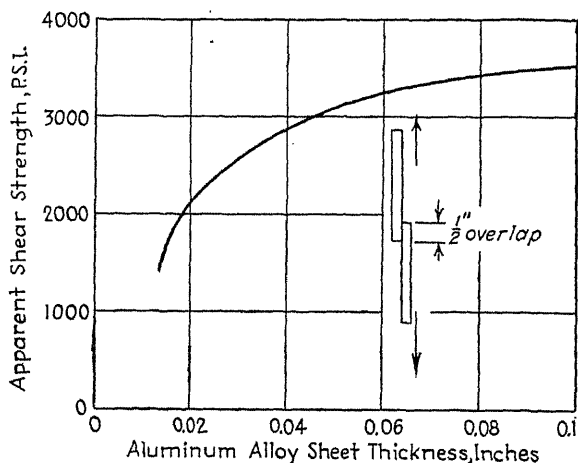


Figure 70. Influence of gage thickness on shear strength of aluminum alloy cemented assemblies.

strength of lower gauge metals, the proportion of normal or tension stresses to shear stresses increases quite sharply. Typical practical results observed upon a synthetic rubber base adhesive for bonding aluminum alloy to itself are illustrated in Figure 70. The apparent shear strength is obtained from the breaking load divided by the shear area of 0.5 sq in.

De Bruyne has also investigated the bonding of metals, and as predicted by the stress analysis of Reissner and Goland, the inflexible cements he employed did not give the expected increase in apparent shear strength after a certain amount of overlap was attained. The results of De Bruyne are shown in Figure 71. However, he also points out that the glue can be stressed more uniformly along its length if the square edges are bevelled off. The tests on overlapped joints bevelled off in this manner show much higher joint strengths for the longer overlaps. Values in excess of 5000

psi were obtained in the application of "Redux" adhesives to steel plate. Some of his results are plotted against the joint factor ( $\sqrt{s/l}$ ) (ratio of the square root of the thickness to the length of overlap). While for ratios up to 3 the mean failing stress is linear, with a relation given by the following formula:

$$p = 10280 \frac{\sqrt{s}}{l}$$

where  $p$  is the apparent failing stress,

the curve flattens out asymptotically to 5900 psi for higher ratios. Results for Alclad, steel, and duraluminum fell on this curve.

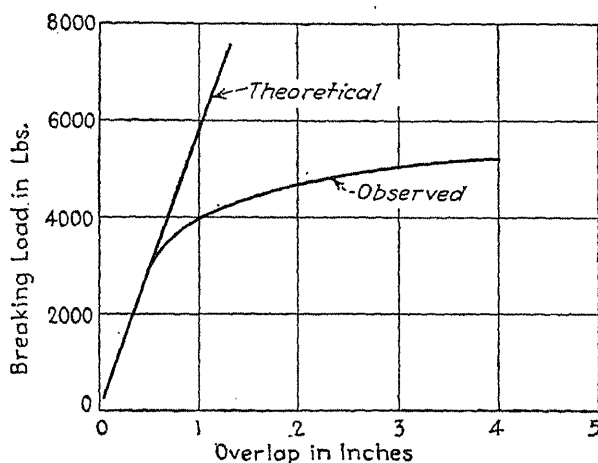


Figure 71. Test on steel strip 1 inch wide and  $\frac{1}{4}$  inch thick (*De Bruyne*).

## Rubber to Metal Assemblies

There has been more work accomplished in bonding metal to rubber than metal to metal, and many developments have taken place in this application in recent years. A number of them were reviewed in the chapter on rubber adhesives, but the more practical aspects will be covered in the following pages. The problem is one of fundamental importance to many mechanical and industrial designs. Reinforcing wire beads in automobile tires must be bonded thoroughly to the rubber; gaskets must be firmly cemented in some instances to their metal flanges; shock absorbing cushions are generally attached to metal faces; and many vibration absorption mounts depend upon metal to rubber bonds, particularly when the energy is carried through the assembly by shear loading, rather than compression loading. With the advent of synthetic rubbers during the war the prob-

lems have multiplied, but adhesives from the synthetic rubbers as well as the natural rubbers are fast solving these problems.

In general there are two main types of cements for bonding rubber to metal: (1) thermosetting resins, which require pretreatments on the metal surface, as well as preparation of the rubber through cyclization, or (2) rubber adhesives which possess good adherence to rubber though the bond to metal surface is more difficult.

There have been many patents covering the bonding of metal to rubber. A few of the more significant ones illustrative of the problems involved are cited in the following paragraphs. Thompson employed phenol-furfural and ground-up rubber for his adhesive<sup>19</sup>. A widely used commercial process for bonding rubber to steel recognized the desirability of applying a pre-coating on the steel surface of a light copper or copper alloy, which improved the adhesion of the rubber. This has been employed on ferrous base tire beading wires<sup>20</sup>. Murphy also applied various treatments on metal surfaces to secure rubber thereto<sup>21</sup>. The advantages of free halogen groups in securing attachment to metal surfaces was recognized by Twiss and Jones who employed such a composition in bonding metal and rubber with a rubber base adhesive<sup>22</sup>. Copper or brass plating prior to securing the metal part to rubber has been recognized as a good pretreatment for aluminum as well as steel<sup>23</sup>. Methods of brass plating aluminum surface after anodizing have been described by Yates<sup>24</sup>. Proske reviewed a number of processes of bonding metal to rubber<sup>25</sup>. Swart gave considerable attention to the bonding of metals to metals with a lap joint and with a thin layer of rubber adhesively bonded in between<sup>26</sup>. These applications were used upon sheet metal sub-assemblies for the automotive industry. He mentioned the cyclized rubber and hydrochloride rubber derivatives as important bonding agents for rubber to metal assemblies. Included were Geer's cyclized rubber (U.S. Patent 1,617,588), Winkelman's hydrochloride rubber (2,139,992 and 2,147,620), and Humphrey's materials (2,144,495). These rubber products are compared more fully in the chapter on rubber adhesives.

Reaney has also developed good bonding agents for rubber to metal adhesion, employing two or more superposed thin films of adhesives of rubber isomers decreasing in hardness<sup>28</sup>. He has developed various adhesives for metals during the past several years. One of the most prominent adhesives for metal to rubber bond is the "Typly" series of adhesives manufactured by the Vanderbilt Company<sup>27</sup>. Applied to the metal surface before it is placed into the mold, the subsequent molding and vulcanization of rubber results in a tight bond. In bonding butyl rubber to metal, a tie stock of precured butyl milled with more sulfur and sheeted, is recommended<sup>27a</sup>.

Pierce brought out further developments in bonding rubber to metal wires by adding a coumarone resin over the surface of the copper plating. This

was followed by a coating of unvulcanized rubber, which during the molding process held firmly to the metal<sup>28</sup>. McBeebe concentrated upon the bonding of aluminum to rubber, both natural and synthetic types. He described various salts which aided the bonding operation<sup>29</sup>. Hosking obtained a better rubber bond to "Monel" metal surfaces which were cleaned and polished than to other metals<sup>30</sup>. "Monel" is substantially a nickel-copper alloy. Gross also worked on the bonding of metal to rubber for automotive applications<sup>31</sup>, using a salt such as cobalt stearate. He has also observed that metal surfaces, which on exposure to  $H_2S$  form dark sulfides, will then bond to rubber satisfactorily<sup>31a</sup>. Sarbrach has found that prime coats of zinc and  $Fe_2O_3$  are helpful in using synthetic rubber cements on metal surfaces<sup>31b</sup>.

In bonding rubber and metal, isomerized rubber was used as the cementing agent and aluminum sulfate and  $P_2O_5$  employed to treat the rubber<sup>32</sup>. The film in contact with the metal was preferably harder than film nearest the rubber being joined thereto. "Styralloy", a rubber-like elastomer of butadiene and styrene was reported as a bonding agent for metal<sup>33</sup>. A rubber-to-metal adhesive has been prepared with the aid of organic diisocyanates and cyclized rubber<sup>34</sup>. The diisocyanates and polyhydric alcohols form polyurethanes which are also good cementing agents.

Considerable study has been given to the nature of rubber to metal bond. No simple relationship has been established between the tensile strength of rubber and its bond strength. In fact for natural and synthetic rubber stocks, maximum bond strength was obtained when they hardened and lost their resilience. The effectiveness of brass plate to rubber was explored in detail, and for optimum results, fresh plating solutions were necessary. Surface concentration of sulfide was an important factor<sup>34a</sup>.

**Treatments of Rubber Surface.** There are various treatments for improving the surface of the rubber to insure a good bond. Cyclization through application of concentrated sulfuric acid is one severe but effective treatment, particularly if a thermosetting adhesive agent is to be employed in bonding to the vulcanized rubber. The formation of various rubber isomers was unquestionably one of the great advances in developing rubber adhesives, and its adaptation *in situ* upon a vulcanized rubber surface to be bonded appears practical in view of the good adhesion exhibited by rubber isomers. After treatment with concentrated sulfuric acid for about 5 to 10 minutes the surface is thoroughly washed and dried. It will be found to be hard and brittle, though this is not objectionable inasmuch as it will form part of the glue line. The adaptation of the "Cycleweld" process to the bonding of rubber is predicated upon this type of treatment. Treatment with concentrated sulfuric acid is also successful upon many synthetic rubbers, except the polysulfide base rubbers which are decomposed.

Exposure of rubber surfaces to actinic rays to increase their tackiness has been suggested by Morse<sup>35</sup>. Griffith also recognized the advantages of preparing rubber adhesive surfaces by heating to high temperatures and reacting with salts of strong acids. He pointed out that the suitability of a rubber to metal bond is determined to a large extent by the plasticity of the material at an elevated temperature<sup>36</sup>.

**Treatments of the Metal Surface.** The careful cleaning procedures outlined earlier in this chapter are to be recommended for steel and aluminum surfaces, as all traces of organic and inorganic impurities should be removed. When thermosetting phenolic or furane adhesives are employed in bonding to metal, good adhesion to the metal surface is not always possible, hence the desirability of applying a primer coating which may adhere well and directly to the metal. Various vinyl resins, acrylics, and cellulose lacquers may be employed for this purpose. This is followed in turn by the thermosetting resin adhesive. Polyvinyl acetate possesses good adhesion to metal surface, which is quite sound and permanent if given a chance to air dry, if applied from solution.

**Bonding Vulcanized Rubber to Metal at Room Temperature.** It is not always possible to bond metal and vulcanized rubber together at elevated temperatures and hence low temperature bonding procedures are sometimes required. One procedure is to apply a thin adhering coat to the metal surface of some thermoplastic resin, and to cyclize the rubber surface with strong acids. The application of cold setting furane resins or resorcinol resins will effect a good bond capable of curing at low temperatures. Longer time is required for this procedure though heating of the metal parts is avoided. Reid developed an improvement in rubber-metal adhesives without requiring a heat curing. Using adhesives formulated on the basis of the rubber isomers, he introduced a non-sulfur vulcanizing agent such as tetrachloroquinine<sup>37</sup>. He obtained A.S.T.M. adhesions of 300 psi between soft rubber and steel and 2500 between hard rubber and steel. Chlorinated rubber has also served as an excellent primer coating on metal for cold bonding metal to vulcanized rubber. Various cements of butadiene-acrylonitrile have also been prepared for vulcanized and unvulcanized synthetic rubber stocks<sup>38</sup>.

The A.S.T.M. method of testing rubber to metal adhesion<sup>39</sup> entails a rubber cylinder measuring 0.5 inch thick and 1.597 inches in diameter bonded between two metal plates with threaded studs. The rubber specimens rupture internally for the best bonds, as the glue line is put into direct tension. Thinner rubber to metal specimens are generally tested in shear. The A.S.T.M. method described above is adaptable to either self-vulcanizing adhesives of adhesives which are set or vulcanized when pressed hot. In the bonding at room temperature, the usual procedure for most rubber ad-

hesives is application to the surfaces to be bonded, then before all the solvent has evaporated, press surfaces together, in order to realize the benefit of the tackiness that is present. On the other hand, the hot press type generally waits until the solvent evaporates to dryness, because heat and pressure generally develop sufficient flow in the vulcanizable adhesive to obtain a good bond.

**Applications.** The combinations of rubber and metal are many, though the chief sponsors of many of the applications have been the automotive and aviation industries. One important application has been extruded "Thiokol" polysulfide sealing tape for aircraft gasoline tanks<sup>40</sup>. Not many rubber-like materials are capable of standing up indefinitely in contact with gasoline. The same strips are used for weatherproofing sheet metal enclosures.

Saunders and Morrison employed rubber adhesives for bonding metal corrugations, applying the cement at the tip of each corrugation and pressing each one individually<sup>41</sup>. A bullet resisting armor plate was developed at the beginning of the war which consisted of sheets of metal bonded to vulcanizable rubber sheets which were cemented in between each layer. These layers absorbed much more energy than a solid sheet of metal<sup>42</sup>.

Other noteworthy applications included spring suspension assemblies with the rubber bonded to metal plates<sup>43</sup>. The rubber could be loaded in compression or in shear. The attachment of acrylic canopies to the B-29 bombers was made possible by synthetic rubber extruded strips cemented to the acrylic plastic edge with either resorcinol formaldehyde or furane resins. These in turn were fastened to aluminum alloy channels for attachment to the fuselage of the airplane. Other large outlets for rubber to metal adhesives include tank car and storage equipments. In these and many other ways, metal-rubber assemblies have been made possible and fully reliable through the employment of modern adhesives.

### **Metal-Wood Assemblies**

The bonding of wood and sheet metal together produces a composite laminate which possesses many advantages from the viewpoint of the wood and metal industries. Metal sheets or even thin metal foils provide a moisture barrier unexcelled by any other organic finish, and are definitely a method of stabilizing wood structure. Even the attachment of surfacing of thin metal foils has many advantages as a moisture barrier. In addition to the protection against moisture, which would be of interest to plywood aircraft and naval vessels, is the fact that metal would reinforce the wood at points of stress concentration and hence it would extend the range of mechanical usefulness of plywood assemblies. On the other hand, wood surfaced metal sheet or metal stampings is still a new material with a num-

ber of industrial possibilities. The chief purpose of applying the wood veneer to the metal is primarily to introduce a surface and a material which lends itself to ready bonding with numerous low cost cements. The bond between the metal and the wood may have been previously accomplished by a strong, high temperature setting adhesive—though once the wood has been welded to the metal surface, the problem is much simplified. There have been various assemblies which benefitted from this combination. For example, the aluminum alloy cover for a fuel tank shown in Figure 72 has been surfaced with a thin wood veneer. Subsequent attachment with a resorcinol or melamine formaldehyde adhesive is made much more simple because bonding takes place to the wood veneer, which has in turn been attached to the metal by a rubber base, high temperature setting adhesive.

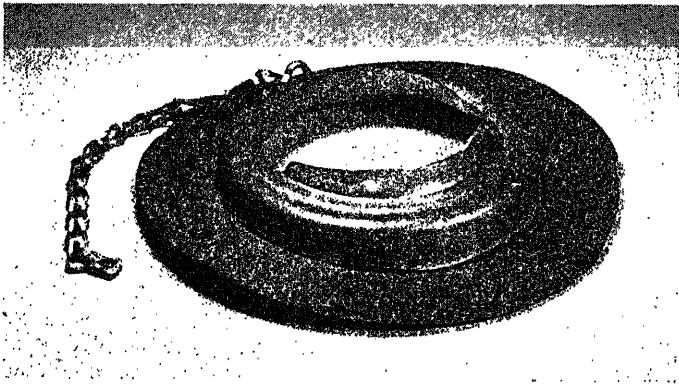


Figure 72. Aluminum alloy surfaced with wood veneer to permit field assembly.

Metal fittings for furniture and numerous cold setting applications of metal bonding are entirely practical by this technique.

The interest in cementing metal faces to wood veneers or to plywood has prevailed for many years. Birch veneers have been faced with sheet metal and bonded with phenolic resin in the preparation of aircraft sub-assemblies<sup>44</sup>. In bonding metal to wood, Ensminger first coated the metal with an alkyd resin to secure good adhesion<sup>45</sup>. Metal reinforcements have been applied to wooden propeller blades using a heat-hardenable adhesive<sup>46</sup>. There have been a number of developments involving metals in wooden blades, for in addition to this, it is a standard practice for certain manufacturers to employ a metal screen at the wing tip of some of their fabricated wooden blades. Metal sheets surfaced with porous adhesive layer which may be cloth or paper are bonded to plywood with a cold-set glue. The porous layer, attached by hot-pressing thermosetting resin adhesives, serves as a base for further assembly work involving the metal sheet<sup>47</sup>. A special

grade of phenolic film, "F-Z Tego," has been produced abroad for bonding aluminum sheet to plywood<sup>47a</sup>.

Staeger discussed the employment of metal faced plywood in electrical engineering applications, citing radio apparatus, switchboards, and motor busses<sup>48</sup>. In radio equipment a continuous metal shield forms a useful screen against radio frequency disturbances. Luty discussed the bonding of a foraminous sheet metal to plywood with a phenolic resin<sup>49</sup>. Steel wires have also been used to reinforce the core of a plywood laminate<sup>50</sup>. It is claimed that these wires contribute to the dimensional stability of the laminate. These laminates have been applied to railway rolling stock. In addition, heater panels are described, in which nichrome electrical resistance wires are imbedded between layers of resin impregnated paper or canvas. These are designed to give off 45 watts per square foot, raising the temperature of the panel to slightly near body heat. Metal wires and cotton fibers, altering directions, have been also employed as reinforcement to rubber and plastics sheet facings<sup>51</sup>.

Plywood faced with a thin metal foil appears to have immediate application to pre-fabricated houses and similar structures according to its sponsors<sup>52</sup>. The material serves as: (1) framework, (2) sheeting, or (3) exterior siding or roofing. Various rubber isomers have been developed to bond metal to wood under heat and pressure. Weatherproofing and flame proofing benefits have also been claimed<sup>53</sup>. Aluminum-low density cellulose acetate-aluminum composite assemblies are also being developed for building construction<sup>53a</sup>.

The bonding of metal to plywood introduces further complications owing to the dissimilar thermal expansion coefficients between the two materials. When a metal panel is laminated only to one side the finished piece tends to warp quite badly, and if both the wood surfaces and the metal side are exposed to the same weather conditions, more warping may occur due to differences in behavior to moisture. For a balanced construction, the metal panel or the metal foil should be laminated to both sides or both faces of the wood. Where structural advantages are sought through the inclusion of the metal facings, the farther they are removed from the core, the stiffer will be the plywood structure for a given weight of material.

One of the adhesive manufacturers recommends a synthetic latex and casein cement which bonds well to metal and retains its flexibility under severe conditions of exposure<sup>54</sup>. As pointed out, dry heat causes the metal to expand and the wood to shrink, a condition which may prove quite detrimental to the strength of the bond. Their procedure is to apply a flexible priming coat and vulcanize it by heating to 285°F. To this priming coat may be applied a number of low temperature setting phenolic and urea ad-

hesives to bond the wood to the metal. Once again a very careful cleaning schedule should be followed to prepare the metal surface for bonding and the adherent coat.

Some of the test results shown in bonding 24ST (Alclad) to wood are as follows<sup>54</sup>, using "Casco NT-442":

Block Shear Tests	Cold Set Urea Resin		Phenolic Resin	
	Load (psi)	Wood Failure (%)	Load (psi)	Wood Failure (%)
24 ST to Maple	3135	45	3560	15
24 ST to Birch	2950	95	2640	25
24 ST to Spruce	1485	100	1685	100

The metals were primed in all cases with a latex-casein cement, and specimens cured at room temperatures and low pressures. The shear strength value is reported, as well as the percentage of wood failure. Structurally efficient laminates have also been prepared from balsa cores with aluminum alloy faces. The grain of the balsa is however, perpendicular to metal facing.

### Metal-Plastics Combinations

Metals have been cemented to plastics for decorative purposes and for providing localized reinforcements. There are a number of examples of combinations of this type. One of the best known applications, laminated table tops, employs a perforated metal sheet in close proximity to the top-most surface. This sheet metal will reduce heat concentrations of burning cigarettes or of hot plates, and by its superior thermal conductivity prevent the plastic from burning or charring. It is the standard manufacturing process to use the thin metal sheets in all table tops prepared from laminated plastics. Numerous assemblies of melamine resin laminates and polyester resins to aluminum sheets have been prepared. These are currently being manufactured for table tops, the plastic laminate offering color and the decorative design details.

Gridley prepared combinations of cellulose acetate sheet and metal with the aid of lactic acid<sup>55</sup>. Kustner also discussed the adhesion problems of cellulose esters upon sheet metal, employing a nitrocellulose base adhesive, containing gelatin and glacial acetic acid<sup>56</sup>. Aluminum foils bonded to screw caps are aided with polyvinyl resin type adhesives. The vinyl lacquers may also be applied as a lining on the aluminum foil<sup>57, 58</sup>. Metal, foil-backed, pressure-sensitive adhesives have related problems in the attachment of the thin metal foil<sup>59</sup>. The adhesion of metal to thermoplastics was found to be aided by a multitude of small depressions or pockets from etched or intaglio cylinder<sup>60</sup>.

Metal is bonded to polyvinyl chloride with a chlorinated rubber cement<sup>61</sup>. The process is claimed to be suitable for both lead and iron sheets. De Bruyne prepared laminated structures of thermosetting phenolics and metal sheets<sup>62</sup>. He further described metal-plastic laminates in a paper, in which he pointed out that the metal sheet was perforated with small holes, with the burrs re-entrant into the plastic. Improvements in flexural stiffness and dimensional stability were the two chief advantages claimed<sup>63</sup>. Stainless steel ornamental designs outside of a paper reinforced laminated phenolic are also suggested. Delmonte also illustrated the attachment of aluminum sheet to Grade C laminated phenolic<sup>64</sup>.

For the greatest flexural stiffness, high strength faces and low density cores possess many advantages. Considerable work is being done along these lines, to offer improved light weight structural materials. Engell and Troxell recommend that the weight of the core materials be two-thirds of the total board weight<sup>65</sup>. In the construction of safety glasses, an improvement has been noted in a protruding plastic interlayer to which is fastened a metal strip for attachment purposes<sup>66</sup>. Phenolic resins and oxidizing agents have been recommended for uniting rubber to metals<sup>67</sup>. A shaped plastic having high resistance to shattering from impact of bullet has been prepared with a center layer of soft plastic in which an open wire mesh floats during molding<sup>68</sup>. Williamson has described sandwich structures using 18-8 stainless steel faces with .063" phenolic asbestos laminated core. The thermal coefficients of expansion of these materials are close<sup>70</sup>.

Rubber to plastics assemblies offer difficult problems because there are not many adhesives which can effect a good bond between these two materials. The difficulties are enhanced for example when the rubber has been vulcanized; but this may often be the case, as for example in the development of certain assemblies for use in contact with fluids, a rubber seal or face may be required upon a solid molded phenolic core. Cyclizing the rubber surface as previously described appears to be a desirable procedure. Then after this treatment cold setting resins such as furane base adhesives will give good results in bonding the two materials together. This combination has been employed in a number of production assemblies.

For illustrative purposes, the table below gives data on the tension shear strength of steel to steel and copper to copper with various low melting alloys<sup>69</sup>. Vibration tests may reveal certain weaknesses of these solders however. Where high temperatures are permitted strong, reliable assemblies may be effected with copper wires and strips, brazing being completed in an atmospheric area. The very high bonding strength attained by the use of special solders or by brazing demonstrates the general superiority of metal bonding agents for metal. Resin and rubber adhesives, while lower in strength, may offer fabrication and assembly advantages.

The cementing of metal sheets together opens further possibilities in

developing superior structural elements, because it makes possible the interleaving of thin sheets together to form a thicker sheet, and building up weight where the greatest stress concentrations prevail. Too often, structures are built of sheets of single thickness and much added weight is carried where not necessary. The lamination of metals with plastics opens the realm of planned structures with the highest efficiency.

Properties of Solders Compared (69)

Alloy	Tin	Composition Per Cent				Melting Point (F°)	Bond Strength, Lap Joint (psi)	
		Silver	Bismuth	Antimony	Lead		Copper	Steel
ST-10	10	1.5		0.5	Bal.	554	4830	4430
ST-16N	16	0.75		1.50	Bal.	511	4280	4330
ST-20N	20	1.25		1.50	Bal.	503	6030	4850
ST-21	21	0.75		1.50	Bal.	503	5900	5400
ST-30	30	1.25	0.5	0.50	Bal.	478	5800	5200
10-90	10			0.50	89.50	568	4960	4090
20-80	20			0.50	79.50	527	5680	4285
30-70	30			0.50	69.50	495	5770	—
40-60	40			0.50	59.50	460	6270	—
50-50	50			0.50	49.50	414	6510	—

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## Chapter 18

### Adhesives for Tapes, Papers, Cloths, and Foils

Tapes, papers, cloths, and foils represent a substantial outlet for the various plastics materials and rubber-like products employed as adhesives. The problems and the requirements depend, of course, upon the functions which the adhesives are to achieve. In some instances a temporary bonding action is required, as for many of the pressure-sensitive type of adhesive—so named because they can be pressed upon many types of surfaces with finger pressure and be made to adhere upon contact. So-called “scotch-tape” is a well known product fulfilling this description.

In applications such as “linoleum cements”, the bond between the flexible sheet material and the floor must be of a more permanent character. Other specialized applications coming under the category of adhesives for papers, tapes, cloths, and foils would be medicinal bandages, gummed labels for bottles, attachment of sound deadening material to ceiling and walls, adhesives for the manufacture of corrugated board, remoistenable adhesives for envelopes and postage stamps, adhesives for bookbinding purposes, the attachment of liners or foils inside bottle caps, masking tapes for the lacquer and sprayed finish industry (a major application in the automotive field), specialty adhesives for advertising displays, decalcomania and manufacturers’ identifications, adhesives for the manufacture of golf balls, various leather and shoe sole adhesives, etc. The list is really interminable, serving many small functions in a large number of applications. The basic requirements are less promiscuous, however, and the bonding problems may be summarized along the following lines:

- (1) *Nature of surface to which adhesive is applied:* Porous (such as cloth, paper, etc.) or non-porous (such as metal foil, film of organic plastic).
- (2) *Adhesion:* Permanently tacky or tacky upon moistening with water or other solvents.
- (3) *Permanency of bond:* Permanently tacky adhesives generally offer temporary bonds, while other types form permanent bonds upon removal of volatiles.
- (4) *Special requirements:* These are qualities such as water-, heat-, oil-, gasoline-, or special chemical-resistance.

The number of adhesive materials which may be considered for the above categories is very large, inasmuch as the ultimate strength requirements are not great, being considerably below those for bonding wood, plastics, or metals. It does not take very much shear strength in an adhesive to produce a bond which will rupture or tear a thin foil or paper. Consequently physical methods for evaluating adhesives for paper, cloths, foils, and tapes differ appreciably from the test methods for structural adhesives. In general, adhesives which are the subject of this chapter are seldom under stress after they have been applied to the surface and set. There may be stresses during setting, when the thin laminae may tend to curl away from the glue line, though, once set in position, the requirements are generally fulfilled. A problem such as creep under stress would not necessarily prevail, although the chemical resistance of the glue and the effect of the adhesive upon the thin laminae it binds are of the utmost importance.

The thermoplastic resins and their plasticizers will be featured in this chapter, as they, more than any other group of adhesives, possess the necessary qualities of tackiness and ease of application. Thermoplastics may be rendered permanently tacky by various plasticizers, though as will be seen in the pages to follow, this may increase the difficulties, *e.g.*, if the backing to which such adhesives are applied is rolled up for storage purposes, the layers will stick together. Non-tacky thermoplastic adhesive films may be wetted by solvents to prepare for application; the general preference in industry is for a water remoistenable type of adhesive prepared from starch or protein base materials. These same adhesives may also be required to be somewhat water resistant to prevent rubbing off from the glass bottles to which they may be attached. The problems are many, though peculiar to the individual application, and at best a general review of major applications and major principles will be attempted so that these may serve as a guide to others working along kindred lines.

### Pressure-Sensitive Adhesives

One of the most popular of adhesive tapes, which began to make its appearance in the 1930's was the pressure-sensitive adhesive tape. This may be truly rated as one of the most outstanding contribution to the art of adhesives. Today every office and industrial plant has made wide use of the pressure-sensitive tapes. Like many good and yet simple ideas, one may inquire as to why this apparently obvious application—namely a tape which could be unrolled and employed for joining two or more thin sheets of material together was not thought of many years before. By examination of the problems disclosed in the patent literature one can see why such tapes have never enjoyed much success until recent years.

Drew contributed much to the art of pressure-sensitive adhesives by his

development of masking tapes for spray lacquering<sup>1</sup>. While his early efforts were to provide means of holding aprons or masks against surfaces towards which lacquers were being sprayed, such tapes found wide usage in many other fields. By means of these tapes it was possible to obtain a clean-cut line of demarcation between different colors. A creped paper backing was selected because it was less expensive than a cloth backing, and because it did not tend to have frayed edges. An adhesive coating was developed which was impermeable to the lacquer solvents, and which when stacked did not deteriorate under ordinary atmospheric oxidation and lose its adhesive powers. A non-drying rubber adhesive was developed which would form a good bond to many surfaces when pressed with the fingers, but one which would not leave an adhesive deposit. Further, when wrapping into a roll, it was not found necessary to introduce a slip-sheeting to prevent one layer from sticking to another. A typical pressure-sensitive rubber adhesive recommended by Drew comprised:

10 pounds of plasticized, clear crepe or smoked rubber sheet  
2 pounds of coumarone-indene resin  
 $\frac{1}{2}$  pound of zinc oxide pigment

The above ingredients are compounded on a rubber mixing roll to a plastic condition and then cut to the desired consistency for application to the tape, by benzol or a petroleum solvent. Before the adhesive is applied to the paper, however, it is treated with a glue-gelatine solution<sup>2</sup>, the purpose of which is to increase the strength of the fibers and adherence of subsequent priming coats. The paper is continuously submerged in a glue-glycerine solution and passed through rolls to remove the excess. This may be followed by treating one side with a dilute formaldehyde solution to insolubilize the glue-glycerine compound. The sheet so treated will be flexible, resistant to shock or tearing, and capable of tight wrapping about many objects. A thin solution of a rubber primer is applied to one surface to make the pressure-sensitive adhesive coating more amenable thereto, while a non-tacky rubber finishing coat is applied to the other side. The finishing coat may be prepared from cyclized or chlorinated rubber and is non-adherent when touched or stacked. Summarizing, the preferred development of the pressure-sensitive adhesive tape follows this pattern:

- (1) Pressure-sensitive adhesive layer (rubber and resin).
- (2) Thin solution of rubber primer which promotes adhesion of the pressure-sensitive layer.
- (3) Paper impregnated with glue-glycerine solution to toughen the structure.
- (4) Non-adherent rubber finishing coat.

In somewhat parallel developments, thin, transparent flexible films of the pressure-sensitive variety were prepared from regenerated cellulose foils, or foils waterproofed with thin lacquers of cellulose esters or cellulose ethers<sup>3</sup>. Particular emphasis is placed upon the primer coating which is composed of partially vulcanized rubber and an admixed compatible resin. The primer coating contains a much higher proportion of resin than rubber (the resins used were wood rosin, coumarone-indenes, and paraffin oil), while the adhesive coating is richer in pure plantation rubber. A better bond is secured to the transparent backing when the primer coat is present. This adhesive tape is characterized by its non-offsetting qualities when applied to smooth surfaces, and can be readily stripped off when desired without leaving behind an undesirable deposit of adhesive. One quick test which would readily prove or disprove the off setting qualities of a pressure sensitive adhesive, is to apply a strip to the window pane and leave facing towards the sun for one day. If on the following day some of the adhesive remains stuck upon the glass it does not measure up to high standards possible with the better commercial goods.

Offsetting qualities are difficult to overcome in a pressure-sensitive adhesive. A cellulose nitrate lacquer film on the surface opposite the adhesive layer represents an improvement over the bare, woven cotton fabric<sup>4</sup>, minimizing the tendency for the tape to stick to itself as it is wound upon rolls. Regenerated cellulose is also used for this purpose<sup>5</sup>, though one of the best protections commercially, is a web of fabric impregnated with gelatine and glycerine<sup>6</sup>. Among other ramifications employed in the manufacture of pressure-sensitive tape is a crepe paper with a parchmentized surface on one side and a partially vulcanized rubber on the other<sup>7</sup>. Chlorinated naphthalene wax and chlorinated rubber on one side of a pressure-sensitive tape, and an adhesive material on the other, form the basis of another product<sup>8</sup>. A flexible backing with a layer of cured or vulcanized rubber will also reduce offsetting properties, and prevent sticking of adhesive when wound on rolls<sup>9</sup>. A surgical tape has been prepared with a pressure-sensitive adhesive on one surface and a pigmented ethylcellulose layer on the opposite surface for waterproofing and reducing offsetting<sup>10</sup>. An adhesive tape of this description is capable of being sterilized, it is claimed<sup>11</sup>. Polyvinyl alcohol and latex have been proposed as a facing for adhesive tapes employing a rubber adhesive layer<sup>12</sup>. Cellulose acetate has also been used to waterproof surgical adhesive tapes, and may be conveniently calendered to one side while the rubber pressure-sensitive adhesive is applied to the other<sup>13</sup>. A hot melt waterproof layer is applied to tapes from a melt of 50 pounds of cellulose acetate, 88 pounds of methyl phthallyl ethylglycollate and 35 pounds of inert fillers, containing no volatile solvents<sup>14</sup>.

There have been a number of other pressure-sensitive adhesive layers than milled rubber which have been suggested and tried in the manufacture of this special type of tape. A protein base for one, has been proposed and applied to an unsized paper saturated with glue and glycerine<sup>15</sup>. Some manufacturers have shown preference for a non-tacky adhesive layer, which may be wetted and activated by an organic liquid; the other face of the flexible fibrous base is coated with a polyvinyl ester. Some of the more highly chlorinated polyvinyl esters are themselves quite resistant to solvents<sup>16</sup>. A non-drying oil such as castor oil has long been recognized as a useful additive to a cellulose derivative in the manufacture of pressure-sensitive adhesives<sup>17</sup>. Instead of continuous layers of adhesive, special wrapping foils have been produced with discontinuous spots or zones of adhesive<sup>18</sup>. Rubber hydrochloride has been recommended as a prime coat for adhesive films of creped rubber and burgundy pitch. The primer is applied from a solution of carbon tetrachloride<sup>19</sup>. Williams and Mitchell suggested a number of thermoplastic derivatives of rubber for the tape problem. They employed a number of phenol-modified rubbers, which were reacted in the presence of sulfuric acid or fluorsulfonic acid. At least 5 per cent of the phenol based on the rubber is used<sup>20</sup>. Chlorinated rubber and a suitable plasticizer are employed as a pressure-sensitive adhesive film in one modification<sup>21</sup>. For a cellulose acetate backing 16 parts of chlorinated rubber, 30 parts of castor oil, and a butyl acetate solvent represent an adhesive formulation, with dibutyl phthalate being used with a regenerated cellulose backing. Alkyd resin elastomers and rosin derivatives have also been employed in manufacture of adhesive tapes (21a). Castor oil and maleic half esters of monohydric alcohols condensation products have also been applied (21b).

Little made a number of recommendations of rosin derivatives for pressure sensitive adhesives of a tacky nature for paper products. Some of these were as follows<sup>22</sup>:

	parts
Hydrogenated methyl abietate	50
Rosin	50
Hydrogenated ethyl abietate	50
Dammar gum	50
Hydrogenated ethyl abietate	40
Coumarone-indene resin	60
Hydrogenated methyl abietate	30
Ester gum	70
Hydrogenated benzyl abietate	70
Rosin	30

Larger proportions of the second components of the above combinations are suited to the various heat-sealing problems. The manufacturers of "Hercolyn" (hydrogenated methyl abietate) have recommended pressure-sealing adhesives from the following general formula:

- 15-20% film forming ingredient chosen from rubber, ethylcellulose, vinyl chloride-acetate, chlorinated rubber, or cyclized rubber
- 20-40% hydrogenated methyl abietate
- 65-85% of rosin, hydrogenated rosin, dammar gum, or coumarone-indenes

Raw rubber and a low acid ester gum have been used as adhesives for transparent cellulose ester films or for regenerated cellulose<sup>23</sup>. With the start of the second World War, as stock piles of natural rubber fell off, the manufacturers of pressure-sensitive adhesives turned to other materials and finally synthetic resins. Polyisobutylene was worked out as a satisfactory agent<sup>24</sup>. Hydrogenated coumarone-indene of a light color was identified as a useful plasticizer for the polyisobutylene. Specialty luminescent adhesive tapes were also developed during the war, comprising ethylcellulose and benzyl cellulose binders; these were used in preference to the cellulose nitrate binders which appeared to destroy the luminescent qualities<sup>25</sup>. Rubber adhesives were also employed for the same purpose. A rubber base and a solid cycloparaffin resin provides a flexible sheet backing with a non-offset, tacky and pressure-sensitive adhesive<sup>26</sup>, according to Tierney. Kemp developed a process of bonding to smooth surfaced non-porous foils of various cellulose derivatives, without the necessity of a primer coating to secure the adhesive layer to the foil backing. He produced abrasion effects on the surface by sandblast or abrading rolls, and then applied the adhesive layer comprised of plasticized crepe and a hydrogenated glycerol abietate ("Staybelite" ester)<sup>27</sup>.

The production of adhesive sheeting from plasticized (tricresyl phosphate) polyvinyl chloride invited special problems of securing a non-off-setting adhesive surfacing layer. Schmidt developed a composition based upon rubber (50 to 75 per cent), polyisobutylene (15 to 30 per cent), and 5-15 per cent of resin from rosin, ester gum, or melted rubber<sup>28</sup>. Schieman described an adhesive tape with five independent layers, comprising the following, which resembles in many respects the tapes previously described<sup>29</sup>:

- (1) Pressure-sealing adhesive layer
- (2) Water- and moisture-proof separator
- (3) Paper base
- (4) Repellant primer layer
- (5) Layer repellant to the sealing adhesive

The problems in the production of pressure-sensitive adhesive tapes are many; the end uses are widely varied. A number of important war time

applications of these products have been described. Ordnance equipment, for example, is protected from high humidity and salt water in overseas shipments through the medium of masking tapes<sup>30</sup>. Improved adhesion to glass, fabric, metal foils, etc., is possible with the many tapes developed for this purpose. Repair of blueprints, drawings, and manuscripts is possible with adhesive tapes possessing a transparent backing. Labelling and packaging can be completed in one operation when the tapes are printed beforehand with the necessary data. Tapes are used for holding rivets during assembly, sealing aircraft instruments, identifying tubes, etc. Some of the specialty adhesive tapes ("Permacel") are applied to cementing assembly operations on thermoplastics, to prevent smearing of the surfaces by the solvent cement; a line of demarcation near the glue joint is made beyond which the cement will not spread. The employment of intricate designs upon adhesive tapes is described by Pendergast<sup>21</sup>.

Various characteristics of adhesive tapes have been the subject of study and standardization by T.A.P.P.I. and the A.S.T.M.<sup>32</sup>. In determining the adhesion between two bodies, one of which is thin and flexible, the simplest test is to measure the force in stripping one from the other. Geer and Westcott described a new linear constant speed rolling apparatus by which strips of tape may be applied to any desired relatively thin flat surface under uniform pressure and time. An apparatus for stripping tests (which resembled a Scott yarn tester) also included a mechanism by means of which the force of separation between the surface and the tape is autographically recorded upon a chart<sup>33</sup>. With these precautions, dependable and reproducible data can be obtained. Specific materials tested included cloth-backed industrial adhesive tape and paper-backed masking tape. In some results on stripping tape from various surfaces, the following data were typical. In all cases the tape was doubled back upon itself and pulled from the surface at the rate of  $25\frac{1}{2}$  inches per minute<sup>33</sup>:

Paper Masking Tape to "Duco" Lacquered Metal Strip

Thickness of Paper Backing (inch)	Stripping Force (ounces)
0.0085	6.5
0.0090	8.3
0.010	12.0

Effect of Weight upon Roller in Applying Tape

Weight Per Inch Width of Tape Applied (lbs)	Stripping Force (ounces)
5	8.8
$8\frac{1}{2}$	9.3
$11\frac{1}{2}$	10.0

By a large number of tests the authors of this work were able to examine masking tapes after they had been run under specific and uniform conditions of aging, and the expected life of the tapes could be arrived at very readily. For certain surfaces which were chemically compatible with the adhesive layer, it could be expected that the force to separate them and the offsetting qualities would be more marked. It appears that if offsetting is to be avoided, the force of stripping the tapes should not be too great. In applications of the tapes, solvents which are deleterious to the backing material or the adhesive layer, should be avoided.

### Corrugated Board Manufacture

The manufacture of corrugated paper board represents a large field of activity in which various adhesives play an important role in assembling components. While in some respects these may be considered laminated products, they are so important from the viewpoint of volume production and box manufacture, that they will not be included under the laminated paper specialties described hereafter. Corrugated board consists of a corrugated sheet core, usually prepared from 0.009 inch thick paper, given a wave-like shape by passing through some corrugating rolls, and corrugations of 36, 52, or 41 per linear foot. Jute or kraft liner board is generally attached to the tips of the corrugations with starch paste or sodium silicate adhesive. When one liner is used, it is called single face corrugated board; two liners, one on either side of the corrugation, is a double faced board. Most corrugated board is converted into shipping cartons immediately after manufacture. By altering the caliper of the sheet stocks employed in its manufacture, bursting strengths and other physical properties may be controlled.<sup>34</sup>

When flexibility in one direction is desired, as a wrapping means and protection for glass bottles being shipped, single faced corrugated board is preferred. For any special requirements of strengths and durability the corrugations and faces may be built up into a wide variety of combinations. Corrugated board for shipping containers overseas requires special considerations, inasmuch as the adhesive employed in its manufacture may lack sufficient water resistance. A great deal of effort has been made in trying to waterproof the corrugated board, both by sprayed interior and exterior coatings of moisture impervious films and resin impregnants for the paperboard stock, though both of these procedures add considerably to the cost. An improvement in resin adhesives was effected with the inclusion of 15 per cent of urea-formaldehyde resin (based on dry weight) to the starch<sup>35</sup>. This improvement was attained with a minimum of change in former operating conditions. A small amount of ammonium chloride catalyst sets the urea resin, developing maximum strength and water resistance. A dry burst strength of 750 psi and a wet burst strength

of 500 psi are obtained. The problem of the adhesive for corrugated boards is peculiar inasmuch as the tips of the flutes are generally coated with adhesive while on one corrugation roll. These flutes are brought into immediate contact with a liner, and then if a double faced structure is being prepared, the opposite flute tips are coated and a second liner brought into contact. The assembly passes over a hot plate which sets the adhesive in a few seconds. The raw starch is actually gelatinized by the heat of the corrugating machine and sets very quickly. One outstanding development in the starch adhesive comprises a suspension of raw starch in cooked starch. Raw starch it will be remembered is capable of giving the strongest joints as compared with cooked starch. While the starch may set quickly, a longer time is required for the urea resin, and most synthetics will not set rapidly enough for this assembly. However, in combination with a material which will set rapidly, an efficient set-up may be realized.

Starch, silicate, and silicate-clay adhesives are the most popular for corrugated box manufacture. The sodium silicate formulations set rapidly by reason of the vast change in viscosity taking place with a few per cent change of moisture—which can be absorbed by the porous paper structure. In some comparative tests upon the mechanical durability of boxes alike in all particulars, Wells observed that corrugated boxes with starch adhesive withstood more punishment than silicate adhesives when testing the containers to destruction in large revolving drums<sup>36</sup>.

The addition of finely divided clay to sodium silicate compositions was an improvement in these materials for adaptation to corrugated board manufacture. Vail and Baker observed that up to 20 per cent of clay reduces penetration and increases the thixotropic effect, improving the adhesive for high speed pasting machines, such as are required in the production of corrugated fiberboard<sup>37</sup>. In developing silicate-clay suspensions, a dilute solution of sodium silicate was employed as a peptizing agent forming smoother mixtures<sup>38</sup>, while Boller employed a dispersing agent such as borax and a high speed colloid mill<sup>39</sup>. The rheological properties of the clay-silicate mixtures determine its suitability as an adhesive in corrugated board manufacture. It must be readily applied from a roll; must have sufficient body to remain momentarily on the tips of the corrugation until the liner or facing is pressed on into position<sup>40</sup>. The performance of sodium silicate adhesives in the manufacture of corrugated fiberboard has been the subject of careful examination. Preferably 18 to 24 pounds of sodium silicate adhesive are applied per 1000 square feet. The heavy liners require more adhesive. Production speeds are in excess of 300 feet per minute<sup>41</sup>.

In addition to the manufacture of corrugated paperboard, sodium silicate adhesives are generally employed to seal the loose flaps of containers that have been filled. The containers, located in the shipping department of

many manufacturers, receive the goods at the end of the assembly line. A quick brush with sodium silicate adhesive ties the flaps together, not holding up the assembly and packing routine.

A development somewhat paralleling the corrugated paperboard was disclosed in a patent seized by the Alien Property Custodian<sup>42</sup>. The invention was related to the manufacture of corrugated plywood. A thin wood veneer, preferably impregnated with synthetic resins, is covered at both faces with a thin layer of paper (see Figure 73). Flat bottom and top webs are glued to the tips of the corrugation. Preference is expressed for a sodium-potassium silicate adhesive mixed with glucose. A honey-combed

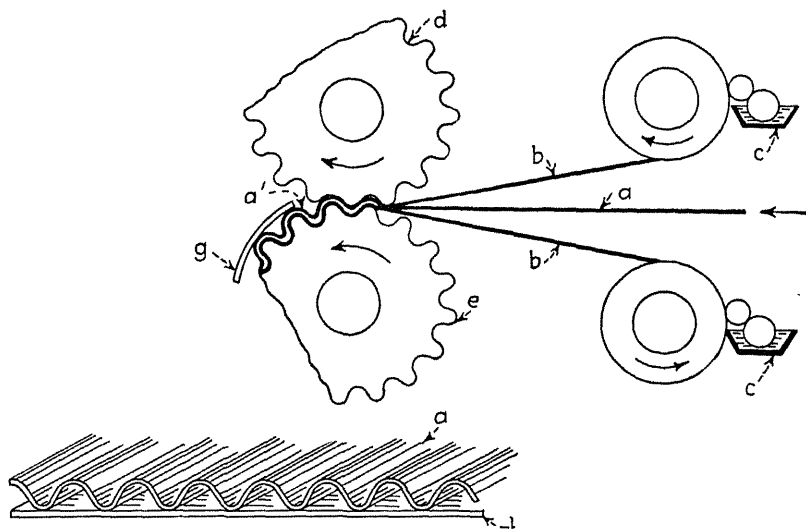


Figure 73. Corrugation of veneer stock.

construction suitable for building purposes is prepared. A lightweight construction material suited for aircraft was prepared by Dornier<sup>43</sup>. Tubular, zig-zags, corrugated, and various honey-combed constructions were prepared of wood, paper, or metal and cemented together.

Another technique of producing a lightweight honey-combed construction is to wrap resin impregnated paper or cloth about tubes of cellophane filled with sand. Surfacing sheets of cloth or paper are introduced and the whole assembly is pressed as one integral unit. When the structure has been bonded together, the cellophane bags are opened at the ends and the sand poured out to leave a series of hollow, trapezoidal openings through the laminate. These special hollow structures have been produced at pressures of 150–300 p.s.i. Among the miscellaneous panels prepared were an all fabric construction, aluminum and creped paper, steel and creped paper

core, etc.<sup>43a</sup>. Both polyester resins and phenolic resins have employed in the preparation of these cores, which may be sliced off to the desired thickness. They serve as excellent stiffeners for aluminum alloy skins for building construction. Competitive to these special low density laminated cores, are the various foams prepared from synthetic rubbers and thermoplastics, which may be as low as 1.5 pounds per cubic foot. Methods of preparing the various foams were reviewed by Sachs<sup>43b</sup>. Various blow agents employed in their manufacture include: 1) Solids yielding gas, b) volatile solvents, and c) soluble gas under pressure.

### Envelope and Label Glues

Adhesives for envelopes and labels have their own special problems; large quantities are used each year. In general the best known glue for this field is classified as the water remoistenable type. The adhesive is applied to the surface of the paper, dried, remaining inactive until such time as moisture is applied from a sponge or a lick of the tongue. Dextrins and starches are frequently found in such adhesive developments. Davidson and Adams concerned themselves with the production of a superior type of adhesive for envelopes. They strove to reduce the tendency of the adhesive to discolor the paper on aging. The cause of the discoloration was attributed to the reaction between degraded protein material present as a sizing agent in the paper and reducing sugars in the paper adhesive. Only partially dextrinized starch was employed, containing not more than 2 per cent of reducing sugars<sup>44</sup>. Various fluidifying compositions have been recommended for combination with the partially dextrinized starch, such as acetamide, propioamide, and polyhydric alcohols<sup>45</sup>.

Edson pointed out that best bonding properties are obtained with native or unconverted starch, though it exhibits the poorest wetting or remoistenable properties. He established a limit of 10 to 20 per cent on dextrin content, with urea as a hygroscopic adhesive activator for use with gummed labels, tapes, and stickers<sup>46</sup>. Back seam gums for envelopes and the transparent window seals are prepared from a cold soluble mixture adapted to envelope machines. Partially converted dextrin, urea (20 to 50 per cent) and a small amount of organic acid are used in the formulation of this adhesive<sup>47</sup>.

Self-sealing adhesives for envelopes have made their appearance at various intervals, though these have not proven as popular as the water remoistenable types. Permanent tackiness and adherence to unwanted surfaces are always basic problems. In one form of self-sealing adhesive, mica powder was added to a rubber latex to form the basis of the compound<sup>48</sup>. Bennett describes several adhesives for envelopes<sup>49</sup>. One of these is typical of the many preparations:

	parts
(a) White dextrin	200
Water	240
(b) Boric acid	2
Glycerine	5
Water	20
(c) Thymol solution—10%	0.5

Dissolve (a) at 90°, add (b), and then ultimately (c). Dulac discusses in detail some of the requirements for paper gumming and the development of paper adhesives<sup>50</sup>. Difficulties in wet weather can usually be traced to some hygroscopic plasticizer. He noted the following features for paper gumming:

- (1) Gums should have a good affinity for water or saliva. The solubility may be enhanced by a 2 to 5 per cent formaldehyde solution.
- (2) Glucose and glycerine decrease brittleness.
- (3) Emulsifying or wetting agents are added in small quantities.
- (4) Counter the brittle character of dextrin by a soft adhesive such as gelatine.

A typical formula for paper gumming recommended by Dulac comprises:

	parts
Water	600
Acid ammonium sulforicinoleate—90%	0.4
Formaldehyde solution—30%	12.0
Dextrin	400

The above is heated to 80°. Then a mixture of 20 parts of gelatin and 40 parts of glycerine may be added. Various salts may be added to increase the speed of setting if desired. In the manufacture of adhesives for postage stamps, gum arabic, as well as dextrans are generally employed. One formula described by Bennett<sup>49</sup> included:

	parts
Gum arabic	100.0
Sodium chloride	2.5
Glycerine	2.0
Starch	2.0
Water	130.0

Another based upon dextrin, and recommended as suitable for postage stamps includes:

	parts		parts
(a) Dextrin	150	<i>mixed with</i> (b) Lime water	10
Sugar	20	Vinegar	40
Water	280		

A problem to consider for most label cements is that of resisting curling during changes in weather, and avoidance of sticking together during hot, humid summer weather. There have not been radical changes in adhesive formulations to fulfill these requirements, and there are not many rules or regulations which govern the proportioning of the different constituents which appear to make one adhesive work and another unsatisfactory. There are as starting materials dextrins, proteins, starches, and water-soluble natural resins, such as arabic gum, though from this point on it has been largely a matter of trial and error. A typical label cement with non-curling properties comprises:

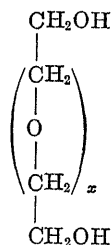
	parts
Casein	1
Powdered mica	1
Boiling water	8.5
Borax	0.25
Sodium fluoride	0.25
Pine oil	0.06

The sodium fluoride makes a useful preservative, particularly for liquid water-soluble adhesives and is present in many formulas of the above types. Many label cements also combine dextrins, sugars, and several polyhydric alcohols, purporting to give dependable performance under humidity extremes. One method of labelling precludes the use of water by forming on the label a dry coating of water-insoluble resinous material and moistening the said coating with a plasticizer solution<sup>51</sup>. Label adhesives for oily surfaces also have special requirements<sup>52</sup>. Animal glues and glycerol are employed as adhesives for decalcomania, sometimes with a minor proportion of mono-butyl-ether of ethylene glycol as a blending solvent<sup>53</sup>. Water-soluble cellulose ethers are also added to envelope adhesives. They will not react with paper to form colored compounds and are miscible with partially dextrinized starch<sup>54</sup>.

Certain adhesives, termed "iceproof glue" are designed for the attachment of labels to bottles. These labels contain animal glue or protein, plus highly water-soluble gel inhibitors such as calcium chloride, urea, or sodium chloride<sup>55</sup>. Water-soluble sodium thiocyanate is also proposed as the gel inhibitor. Paper labels for medicinal purposes of the U. S. Army are required to withstand submersion in tap water for 48 hours, followed by 24 hours' drying and not more than 25 per cent separation of the glued area<sup>56</sup>. Stilwell developed a gummed sheet of water remoistenable adhesive in a continuous phase and a deformable resinoid filler in a discontinuous phase, with a ratio of 2 parts of adhesive to 1 of filler<sup>57</sup>.

Polyethylene glycols and "Carbowaxes" appear to be useful additives to envelope and gummed paper adhesives, stabilizing the moisture content

and keeping the paper from curling<sup>58</sup>. These comprise a series of products that include both liquids and wax-like solids. All are unctuous, but water-soluble, a combination of properties which will influence the development of adhesives for paper products. These compounds have the following general formula:



Chlorinated starch, casein, nitrocellulose, and polyvinyl acetate compounds are compatible with these compounds, and are plasticized by the polyethylene glycols.

Herman and Knowlton contributed an interesting paper on methods for evaluating starch base adhesives for bottle labelling and case sealing. Viscosities were evaluated with falling ball viscosimeters and films examined for hygroscopicity, color, plasticity, and adhesive strength<sup>59</sup>. Not much comparative data were reported though test methods were outlined in some detail.

The application of labels to glass packages requires much care in the selection of the correct type of adhesive and the proper regulation of the labeling equipment. There are various methods of labelling glass bottles, including the following:

**Hand Labeling.**—The labeling paste is spread over a table top, while the labels are placed downward on the material to soak and temper. The labels are applied by hand, and then wiped with a soft, damp rag.

**Table Gumming Machines.**—The labels are fed by hand or automatically to a gumming machine which applies correct amount of adhesive. They are then immediately placed by hand upon the glass package.

**Automatic Labeling Machines.**—When the glass bottles and the labeling devices are synchronized together, greater speed of production may be realized in the correct automatic equipment. Fast setting glues are employed. The labels are either picked out of the hopper by vacuum or glued stencils.

Paper stock for labels is generally 50 to 60 lbs (ream weight basis). The adhesive may strike through thinner stocks, while the heavier stocks do not conform to the shape of the jar or bottle too readily. Grain direction of the label is preferably horizontal, running side to side, according to the

opinion of some of the leading manufacturers for bottle label adhesives<sup>59a</sup>. This reference also discusses in detail the more common labeling difficulties and their remedies, including: Labels curling away from bottles; wrinkling or blistering of labels; failure to pick labels out of hopper; spotty adhesion; tearing of labels in the automatic machines; labels falling off of bottles; scuffing of labels while nesting; difficulty in removing labels; crooked labeling; discoloration of labels; etc.

### Laminated Papers

A large number of laminated specialties have been prepared through combinations of thin papers and foils with one another. These have been used largely for special packaging requirements, and represent many unusual bonding problems. DeSylva prepared an interesting paper on the methods of applying adhesives to thin foils, illustrating these with various sketches<sup>60</sup>. Among the methods he described were: (1) reverse roll coating, (2) modified direct roll coating, (3) Meyer bar roll coating, (4) dip, two side roll coating, (5) direct roll coating with levelling bar, (6) roll coating using two steel rolls and levelling bar, (7) slot pressure extrusion applicator, (8) gravity or pressure feed knife coating on hard surface cylinder, (9) gravity feed drill rod, (10) knife coater between adjustable rolls, and (11) pressure extrusion coating between adjustable rolls.

Southwick reviewed the art of laminating specialty papers, pointing out that by lamination it was possible to form structures with a wide variety of functions, depending upon the individual plies used in developing the laminate. Two plies of glassine paper with a waxy laminating agent formed a pliable, low moisture vapor transmission assembly. Other combinations described included lead foil to paper to cloth; laminated kraft to kraft to cloth; cellophane to cellophane; aluminum foil to cellulose acetate; and many others. He prepared a table describing the functions of various adhesives, which is reproduced herewith<sup>61</sup>:

Type	Example	Function
Aqueous emulsion	Dextrins, glues	Greaseproof, strength
Emulsion	Rubber latex	Limited waterproofness
Solvent solution	Resins or gums	Greaseproof, waterproof
Heat liquified	Wax, asphalt, or resin mixtures	Greaseproof, waterproof

Many types of adhesives have been used at one time or other in preparing laminated papers and a few of the many types are described in the following paragraphs. Dreyman used an amorphous petroleum wax carrying as a suspended colloid phenolic, alkyd, or copal resin<sup>62</sup>. These united sheets of paper to make them suitable for packing. Petroleum wax and ester gum

dissolved in coumarone-indene or phenolic resins were suited to the bonding and waterproofing of cardboard<sup>63</sup>. Much of the latter is made from a low cost chipboard prepared from ground-up newsprint. A paper fiber container for packaging milk presented various problems of gluing as well as sealing. Paraffin wax worked out quite satisfactorily for this purpose, usually being applied by dipping the container down into a hot melt of wax<sup>64</sup>. The bonding of regenerated cellulose film to itself has always presented a problem and while gelatine and water may serve the purpose in some instances, moisture-proof cellophane has a heat sealable coating applied to the outside, which is useful in obtaining adhesion. One type which has been suggested is prepared from<sup>65</sup>:

	parts
Gum acacia	16.5
Glycerine	29.5
Water	49.5
Formaldehyde—40%	4.5

In laminating glassine paper, Barnhart employed the following<sup>66</sup>:

	%
Paraffin wax	40-63
Rubber	3-12
Petrolatum	7-13

Edson and Mach prepared cold water-soluble adhesives for paper and cardboard from 100 parts of partly converted dextrin, 40 parts of urea, 28 parts of sodium chloride and 80 parts of water. Urea and sodium chloride act together as a dispersing agent for the dextrin, without distortion of surfaces to be joined<sup>67</sup>. The adducts of terpene and maleic anhydride reacted with glycols have formed strong, flexible adhesives suited to paper, cloths, and foils<sup>68</sup>. Quick-setting polyvinyl alcohol adhesives suited to the laminating of paper, cellophane, leather, cloth, or wood have been prepared from a dispersion of unhydrolyzed starch in a 3 per cent solution of polyvinyl alcohol<sup>69</sup>. Advantages claimed for the polyvinyl alcohol were resistance to vermin and no chemical effect on the sizings in the paper.

The assemblies of paper containers for liquid food products have been made possible with a hot melt adhesive prepared from polyvinyl acetate and dammar gum<sup>70</sup>. These joints do not open even when dipped into hot paraffin wax at 190°F, applied for waterproofing purposes. A parchmentized paper having a layer of rosin sizing agent may be bonded with a thermoplastic adhesive layer of paraffin wax and pale crepe rubber<sup>71</sup>. With the shortages of tin at the start of the second World War in 1942, manufacturers turned to laminated paper packages combining outside

opaque and chemically resistant layers, and inside stiff paper cores. Waxes, synthetic resins, and cellulose derivatives were employed as laminating agents<sup>72</sup>. Those thermoplastics which soften with heat and are capable of adhering by heat sealing methods are often sought for small paper packages<sup>72</sup>. Foils of polyamides have also been laminated together to form chemical and heat resisting assemblies<sup>74</sup>.

Laminated paperboard stock has been prepared into relatively thick walled tubes suited for mailing cartons, cylinders and the like. Starch and sodium silicate adhesives are generally applied at the time the paper stocks are wrapped helically into the tubular shape. A few hot setting binding agents have been employed, such as "Vinsol", which is the gasoline insoluble fraction from pine wood rosin<sup>75</sup>. Approximately 10 per cent of zinc oxide increases the melting point of the "Vinsol", which at the time of pressing is fused into intimate contact with the cellulosic fibers. Rubber adhesives have also been used for convolutely wound paper tubings<sup>76</sup>.

A laminated foil of thin aluminum is coated with 98 per cent of asphalt and 2 per cent of rubber adhesive composition. When wrapped a thin paper separator is necessary<sup>77</sup>. Cleaveland discusses the coating of various papers with plastic films. Early efforts resulted in the adoption of decorative cellulose nitrate coatings, though more stress recently has been placed upon heat sealing coatings to eliminate the wet pastes ordinarily used. An increase in ream weight of 2 to 5 pounds is all that is required from a material standpoint<sup>78</sup>. Improved resistance to moisture vapor transmission can also be applied to conventional papers by plastic coatings. Mitchell developed a heat sealable Cellophane sheet by a coating of polyvinyl acetate, cellulose nitrate, and diethylene glycol monomethyl ether<sup>79</sup>. Good oil and grease resisting properties can also be expected. For waxed papers, added difficulties present themselves, though an adhesive is claimed in an aqueous dispersion of corn syrup and rubber<sup>80</sup>. To 100 parts of 60 per cent latex is added 25 parts of corn syrup and 2 parts of sodium lauryl sulfate. After application to each surface they are partly dried and then pressed together.

Bauer developed a number of starch adhesives for bonding paper<sup>81</sup>. He employed combinations of chlorinated starch with white tapioca starch, urea, corn sugar, water, and citric acid. Incompletely dextrinized wheat starch was also used. Wall paper coatings and adhesives were developed from these. In another wall paper adhesive, calcium carbonate (1 to 5 microns) was dry milled with 1 to 2 per cent of casein or soya bean protein for 3 hours<sup>82</sup>. For asphalt impregnated plyboard, an adhesive comprised of ungelatinized starch in a gelatinous carrier and an emulsified asphalt (0.5 to 10 per cent) provided good bonding qualities<sup>83</sup>. Solutions of cellulose ethers have been employed in wall paper hanging<sup>84</sup>.

The problems and the variety of materials being bonded are many. In the years to come we will most likely see an increased use of very thin aluminum foil for many of these special laminated paper constructions. The aluminum foils provide an excellent barrier to moisture and have an inherently good chemical resistance. Many of the problems of special paper laminates are applicable to the development of liners for bottle caps of liquid chemicals and foodstuffs. An outer film or coating of polyvinyl chloride-acetate has generally been popular in withstanding various chemicals and food acids.

**Bookbinding Adhesives.** Many of the paper adhesives already described have been employed in the binding of books, magazines and their covers. Low cost, easily applied, cold setting adhesives are preferred, and materials such as animal and fish glues, starches, and protein base adhesives have been widely used. These are not as sensitive to temperature for their time of setting as are the various catalyzed synthetic resin types. Rasmussen developed a strong fast setting adhesive for bookbinding from rubber latex with a suspension of casein. The ultimate proportions of water, casein, and latex are adjusted so that critical ratio of water to casein is below that causing breakdown of the solution<sup>85</sup>. The bookbinding adhesives are generally applied manually from a glue pot, made up fresh each day for the work immediately ahead.

Bennett<sup>49</sup> (page 16) describes several bookbinding adhesives. One of these dissolves potato starch in a calcium chloride solution, while another makes provisions for changes in the season as follows:

	Winter (%)	Summer (%)	Mid-season (%)
Glue	30.9	35.7	33.3
Sorbitol (83%)	15.45	10.7	12.54
Glycerin	5.15	3.6	4.16
Water	48.5	50.0	50.0

A flexible bookbinding adhesive is described in a Canadian patent<sup>86</sup>:

	parts
Glycol bori-borate ("Aquaresin")	8.0
Bone glue	6.0
Glycerin	4.0
Spermaceti	0.4
Water	12.0

A government publication on the subject of flexible glues for bookbinding places emphasis upon various formulations of animal glues<sup>86a</sup>. As a result of numerous laboratory tests and years of performance tests in the bindery,

a single grade of high gel strength and high viscosity animal glue was selected. It is pointed out that the cost of the glue is not the correct basis for evaluation, but rather in the quantity of water it will absorb without loss of essential adhesive properties. With glues of high gel strength, larger proportions of flexibilizing agents may be used. Glycerin and sorbitol are added to develop the desired flexibility. The proportions recommended in this publication upon bookbinding glues are as follows:

General Bindery Use.—

Animal glue	20.80
Glycerin	16.60
Waste Roller Composition	9.80
Water	52.50

Use on Gathering, Stitching, and Covering Machines.—

Animal glue	36.30%
Glycerin	16.60
Water	46.80

Tablet Composition.—

Animal glue	26.50%
Glycerin	26.50
Water	46.70

In all of the above formulas, as well as those listed below, .15% beta naphthol functions as a preservative against formation of bacterial molds, and .15% terpeneol is added to mask any unpleasant odors. When shortages developed in glycerin, sorbitol served as an excellent replacement. While in pure form, sorbitol is a white crystalline substance melting at 97°C., an 85% sorbitol syrup is generally purchased for production. Typical formulas involving the use of sorbitol are:

General Bindery Use.—

Animal glue	22.60%
Sorbitol syrup	20.50
Water	56.60

Use on Gathering, Stitching, and Covering Machines.—

Animal glue	36.40%
Sorbitol syrup	16.60
Water	46.70

For Gluing large thick books, previous to rounding and backing.—

Animal glue	22.50%
Sorbitol syrup	25.90
Water	51.30

Sorbitol is a very effective hygroscopic agent, having a narrower humectant range than glycerin, and hence is less susceptible to changes in humidity. Higher viscosity book binding glues are experienced with sorbitol, though slightly longer setting times may be required. It is recommended that after the glues are cooked together at temperatures about 150°F., they be poured into slabs and stored at approximately 55°F. until ready for use<sup>86a</sup>.

### Paper Impregnants

The impregnation of paper stock with various resins results in a greatly improved wet strength, and in some cases the adhesive may contribute to the dual rôle of an impregnant as well as adhesive. However, the most successful results have been obtained upon the addition of resin to the wet paper pulp, forming the resin *in situ* in the paper stock. In reviewing some of the work in this connection, that of Schur may be noted whereby a paper web is dried and impregnated with a casein binder in aqueous ammonia. The web was passed between rolls and dried at low temperature, followed by a high temperature cure for a few seconds. The wet burst strength of the paper is greatly improved<sup>87</sup>. Even more outstanding results were obtained upon the addition of small amounts of acid catalyzed urea or melamine formaldehyde resins to the wet pulps. The pH was adjusted to 4.5 to 6.0 and exceptionally good wet strength developed in the final paper stock. It only took about 3 per cent addition of synthetic resin to achieve this marked improvement in wet strength of paper<sup>88</sup>, up to 50 per cent of dry strength. The folding resistance of the paper is also greatly improved. While the melamine resin is added to the wet slurry of cellulosic fibers, it is reported that between 70 to 90 per cent of the added resin is retained on the fiber, comprising up to 5 per cent of the total weight. Urea formaldehyde resins are also added to paper stock for the same purpose<sup>90</sup>. These developments are, of course, distinct from the manufacture of full resin impregnated laminated stocks, where 40 to 50 per cent resin content may be present. The small percentage of resin added to improve the wet strength, does not stiffen the paper, or change its appearance.

### Leather and Linoleum Adhesives

Adhesives for leather and linoleum products require greater strength and durability than many of the adhesives described so far in this chapter, because they bond stronger materials together and must withstand severe service conditions. While scrap leather itself may be treated to prepare adhesive-like materials, thermoplastic polymers are generally preferred. Animal glues, flexibilized with glycerine have been used for many years

for this purpose, with improved water resistance being obtained upon the addition of formaldehyde and potassium bichromate. Water resistant casein adhesives and rubber adhesives are also employed, though cellulose esters are used a good deal. The latter are commonly known in shoe manufacture, combining good water resistance with oil resistance. Typical leather cements for shoe soles are formulated along the following lines:

	% by weight
Cellulose nitrate	18-20
Solvents	65-70
Plasticizers	10-20

Typical rubber cements for leather goods are formulated along the following lines:

	% by weight
Pale crepe rubber	10
Powdered rosin	50
Solvent	40

Various self-vulcanizing rubber cements (see Chapter 8) may be prepared for the attachment of rubber soles. The usual procedure is to apply to surfaces to be joined, wait a few minutes and then press together firmly while surfaces are still tacky. While heat has been used in setting cements used in bonding leather shoe goods, as in the adaptation of high frequency heating to this problem<sup>91</sup>, cold setting cements are widely employed both in field and factory. For solid or paste-like leather adhesives, petroleum pitch is a useful compound, though for the liquid types plasticized rubber varieties are popular.

In the bonding of the leather substitutes, as in the assembly of decorative book covers, animal glues, casein adhesives, and nitrocellulose derivatives may be found. Of course, the cement must set quite rapidly, as the parts cannot be placed under pressure for any length of time without tying up expensive jigs and fixtures for just one assembly operation. In general the thermosetting resins are not to be desired for bonding leather, inasmuch as they are too stiff when cured, and the more flexible room temperature setting thermoplastics are preferred. Menger observed that when halogenated, polyvinyl chloride was effective as a leather adhesive<sup>92</sup>.

Linoleum cements are generally low in cost inasmuch as considerable quantities must be employed in the placement of the floor covering. The surfaces to which linoleum is to be bonded are not always smooth and may be quite porous, requiring considerable quantities of adhesive to fill up the hollow spots. In consequence, adhesives such as sulfite waste liquors and coumarone-indene resins are employed frequently in the manufacture of these compounds. Asphaltic base compositions may also comprise

the binding medium. In one typical example 15 to 40 parts of asphalt, 17 to 30 parts of pitch, 4 to 10 parts of Gilsonite, and 45 to 55 parts of powdered silica are employed<sup>93</sup>. Oxidized drying oils provide the base in still other compositions, as for example the following<sup>94</sup>:

	%
Oxidized drying oil	27-35
Rosin	6-8
Filler—bentonite clay and asbestos	35-40
Solvent—alcohol	25

On the other hand rubber compositions are always popular because of their high initial tack, and raw rubber and rosin are employed for this purpose<sup>95</sup>. Coumarones offer good possibilities inasmuch as there is a wide assortment of softening points to choose from. A typical formula employing coumarones, has the following proportions<sup>96</sup>:

	parts
Coumarone-indene (m.p. 100-115°)	25
Coumarone-indene (m.p. 20-30°)	2.8
Portland cement	57.2
Asbestine	4.6
Acetone	2.1
Methyl ethyl ketone	8.3

Jeschke employed animal glues and glycerine with an added phenolic resin as binder for linoleum<sup>97</sup>. Urea resin adhesives have also been suggested for linoleums<sup>98</sup>, as have polymerized rosin and oxidized drying oils<sup>99</sup>. Other linoleum adhesives involving coumarones were suggested by Daimler and Throw<sup>100</sup>. Sigler and Martens presented a good report on the properties of adhesives for floor coverings<sup>101</sup>. Their investigation covered the adhesives and primers used for bonding linoleum and other floor coverings to sub-floors. Tests were made to determine the resistance to straight pull and a stripping pull upon bonded  $\frac{1}{8}$  inch battleship linoleum to concrete, wood, and metal. Tests were conducted before and after exposure to moisture, and while previous tests were conducted upon dry sub-floor, damp concrete invited special problems<sup>102</sup>. Satisfactory installations over concrete subfloors in contact with the ground have not been too consistent, inasmuch as heating and cooling effects may develop quite a vapor pressure immediately under the floor covering. Asphalt tile and asphalt cements have met with fair success, though not always under damp conditions. The following table is reproduced directly from the report of Sigler and Martens<sup>101</sup>. The straight pull represents the results of a straight tension pull, while in the stripping out test, the specimen is folded at a 90 degree angle to the plane of the surface, and pulled upwards normally to the surface:

## Adhesive Strength Tests with Linoleum

Adhesive	Straight Pull 4 square inches area					Stripping Pull 2 inch width		
	Dry			Exposed to Water		Wood (lbs)	Steel (lbs)	Con- crete (lbs)
	Wood (lbs)	Steel (lbs)	Con- crete (lbs)	7 days Con- crete	14 days Con- crete			
Lignin paste	249	378	268	0	0	5	6	4
Copal resin	252	248	308	125	—	9	4	7
Cumar resin	294	285	345	275	206	12	12	12
Rosin and petrolatum paste	20	16	27	20	23	0	—	—
Casein-latex	399	325	429	93	—	28	10	31
Alumina cement and latex paste	336	360	362	220	232	16	—	—
Rubber dispersion cement	—	—	104	—	71	—	—	—
Portland cement and cellu- lose nitrate dope	—	—	187	92	—	—	—	—

Various primer coatings of phenolics, rubber, coumarones, and alkyds were applied to the top surface of the concrete and while some improvement was noted in withstanding the moist concrete, no permanent solution was forthcoming in this direction. The report recommended a bituminous impregnated membrane placed between two concrete slabs to insure best conditions of moisture protection. Such an installation can be made cheaply at the time of construction. Asphaltic concrete of sufficient thickness will also serve as an adequate moisture barrier.

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## Chapter 19

### Adhesives for Inorganic Materials

Adhesives for ceramics and related inorganic products may be formulated from both organic and inorganic substances. In some instances the adhesive must fulfill the rôle of a sealing agent as well as an adhesive, in order to reduce the porosity of the product. Usually, however, a strong, permanent bond is required. The bonds may be required to withstand corrosive chemicals, or very high operating temperatures. The number of adhesive applications to inorganic products is indeed quite multifold; e.g., as binding agents for abrasive grains used in the manufacture of grinding wheels; in the manufacture of safety glass; and for the attachment of one fire-brick to another (usually called luting).

Many of the adhesives employed in these operations were discussed in earlier chapters dealing with the individual resins. For example, various synthetic resins have been cited from time to time as binding agents in the manufacture of grinding wheels or abrasive papers, and while the subject will be re-examined, this time it will be approached from the viewpoint of the grinding wheel manufacturer, rather than that of the resin manufacturer. In addition, other important inorganic applications will be discussed, particularly chemical stoneware, which is of the utmost importance to the chemical processing industries, inasmuch as the assembly of various fired bricks is a cementing operation requiring careful skill. In fact, many of the earliest adhesive problems entailed the employment of inorganic products as the medium for cementing. Portland cement, clay, "adobe" mud, and related products are well known in building construction.

The subject of household cements for broken dishes, pottery, and the like, will be briefly mentioned because of widespread interest in this direction, and new and important combinations of ceramics will be suggested in connection with dissimilar materials such as metals and plastics. The scope of adhesives for inorganics may also be extended to include such large volume applications as the uniting and sealing of ceramic sewer pipes—a subject of current interest and of major importance from a health standpoint. Vegetable growths have played havoc with many cemented joints and the optimum in sealing and cementing techniques is still to be desired.

Another problem arises in connection with the placement of linoleum and the like upon concrete floors. Adequate sealing agents against the penetration of water are difficult to find. The sealing agent may serve as the binder for linoleum, though more usually the adhesive agent is separate from the sealer coat. In other fields, special optical cements for mounting lenses have been the subject of much investigation, with some of the newer synthetic resins meriting attention.

The selection of an inorganic cementing agent as against an organic type depends a great deal upon the requirements of the application. Because much of the ceramics ware is to be employed at high temperatures, the high temperature resisting inorganic cements would have preference. On the other hand, in order to reduce porosity, organic types are often employed for their sealing action. Regarding the inorganic cements, many of the formulas which have appeared, reflect trial and error rather than a carefully organized approach to the specific problems of adhesion. The literature is replete with different proportions of ingredients used for various cementing agents, though little or no data illustrating the influence of variables in composition upon the ultimate properties.

### **Cementing Agents for Chemical Stoneware**

Inorganic and organic cementing agents are widely found in chemical stoneware assembly, electrical refractory binding materials, and repairs or assemblies of ceramic ware. Many of these formulas are based upon the following binders: sodium silicate; magnesium oxychloride; sulfur base; Portland cement; resin cements and miscellaneous types. In the chapter on miscellaneous sodium silicate adhesives, the requirements of this type were examined; at this time, the specific applications to chemical stoneware will be reviewed. With the decrease in alloy metals at the start of the second world war, a greater share of attention was given to ceramics and stoneware by chemical processing industries, and their assembly involved a liberal use of various adhesives.

**Sodium Silicate Cements.** Sodium silicate cements have been used for many years as bonding materials for chemical ceramic ware. Their principal use is as a mortar to butter bricks as they are laid up one upon another to form a lining for some tank. Acid-proof bricks which are used in the manufacture of the lining are subject to a process of vitrification which renders them inert to chemicals contacting them. On the other hand, silicate cements cannot be subjected to a firing process and are more subject to attack by the chemicals to be handled.

Sodium silicate comes in both powdered and liquid form. The water used to make a paste or solution of the sodium silicate does not enter chemically into the hardening process and as it is removed by evaporation or diffusion, the cement tends to shrink and become porous. This is a

disadvantage when the tank is to contain solutions which may infiltrate into the pores of the cementing agent. Consequently, most formulations employ some fillers to reduce porosity, and the joints are kept as thin as possible between bricks ( $\frac{1}{16}$  to  $\frac{1}{8}$  inch), according to Barr<sup>1</sup>. Moore emphasized the importance of selecting suitable cement for the connecting links in chemical plants. Among the sodium silicate types which he described are the following<sup>2</sup>:

Cement	Approx. Max. Temp.	End Use
Sand (1) Asbestos (1) Sodium Silicate Solution (2)	150°	Acid and salt solutions
Barium Sulphate (3) Asbestos (1) Sodium Silicate Solution (2)	150°	" "
Sand (11) Powdered Quartz (17) Sodium Silicate Solution (7)	500°	" "
Powdered glass or sand (1) Portland Cement (1) Sodium Silicate Solution (1)	100°	Halogens (liquid)
Fireclay or powdered brick with sodium silicate solution to a paste	1400°	Furnace parts and attachment of metal conductors to refractory tubes

The above cements depend largely upon the binding qualities of sodium silicate, and considerable time may elapse before they become fully solid. Further developments in acid-proof cementing agents from sodium silicate solutions led to the incorporation of acids or acid forming salts. These compositions formed the basis of the so called self-hardening types. Of course, too rapid setting qualities proved undesirable, though cements were prepared with pot lives suited to the jobs on hand. These adhesives proved to be most serviceable under conditions of strong acid concentration, in fact improving in performance. They are not suited, however, to the handling of hydrofluoric acid. To illustrate a few trends in this direction, the following examples of self-hardening sodium silicate cements may be noted:

	parts	Use
Powdered quartz	62	Recommended for glass to metal cement <sup>3</sup>
Sodium silicate	14	
Water	14	
Aluminum fluoride	10	

Powdered sand or glass	100	
Kaolin with sodium silicate solution to a paste	5	Fixing glass or stoneware or fused silica tubes into metal sockets for acids or salt solutions <sup>2</sup>
Oxalic acid	1	

A fast setting acid proof cement is prepared by mixing (a) of the formula below, with the constituents in (b)<sup>6</sup>:

	parts
(a) Benzoic anhydride	20
Silicate powder	980
(b) Sodium silicate solution	300

Reaction of alkali silicate with alkali titanium fluoride will also form a fast setting acid proof cement<sup>6a</sup>.

The preparation of cements for assembly of ceramic components generally entails the addition of the siliceous powder to a sodium silicate solution, while for the refractory high temperature resisting cements, solid sodium silicate is combined with silica powder and mixed with water on the job. It is important to keep such preparations thoroughly dry, because the absorption of water or carbon dioxide before mixing will decrease their ultimate strength. These types do not shrink as much as the cements prepared with the aid of sodium silicate solution. In the self-hardening varieties, the presence of the acid precipitates the silica and forms a bond to the materials being joined. There is a further advantage in that the sodium silicate is no longer water-soluble. Sodium silicate cements are not generally recommended for alkalies, except for certain of the quick-setting cements which are self-hardening.

**Sulfur cements.** Among other industrially important cements which withstand corrosive liquids and gases are those based upon crystalline sulfur. These are limited in temperature, of course, but give a sound non-porous joint. They adhere quite well to acid-proof bricks, and materials such as rubber and asphalt. They are generally applied by melting and pouring into gaps which are left purposely wide, and which are sealed off to prevent loss of the cementing agent. The large volume of cement keeps the joint hot and the material fluid enough to fill all the crevices. There is some contraction during cooling, though by the proper technique this may be compensated for: by applying some pressure on the joint while it is setting or else, by pouring slowly to fill the gaps. Most of the cements melt around 235°F and in the event of temperatures elevated to 200°F, provisions should be made for the expansion of the joint in order to avoid loss and decrease in mechanical strength.

One important proprietary sulfur cement contains a small amount of olefine polysulfide synthetic rubber<sup>4</sup>. The proportions are as follows:

	parts
Polysulfide ("Thiokol")	4
Sulfur	36
Sand	60

This composition is employed for pipes and tiles of pickling tanks quite successfully.

While sulfur cements have been known for a good many years, credit to Bacon and Davis is due for citing the possibilities of employing the sulfur cements in chemical processing equipments<sup>5</sup>. Numerous applications followed their work, and with the contributions of Duecker<sup>4</sup>, the art moved forward quite rapidly. The problem confronting Duecker particularly was the apparent failure of sulfur cements under certain unexplained conditions, later evaluated as thermal shock. The addition of a small

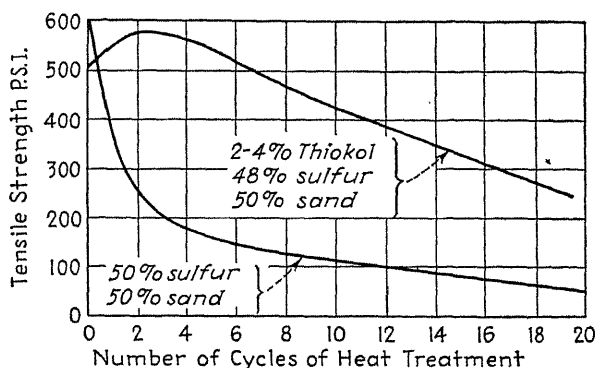


Figure 74. Effect of thermal shock on physical properties of sulfur cements (Duecker).

amount of "Thiokol" to the sulfur-sand admixtures improved this characteristic considerably. Using a test cycle of alternate exposures to 84° and 4°, the physical properties of various sulfur cements were evaluated, and some of the results are disclosed in Figure 74. In fact after 3 cycles of heat treatments, properties are slightly improved over the original behavior, when a small percentage of "Thiokol" is included<sup>4</sup>. On the other hand, the flexural strength falls off to some extent as the synthetic rubber modifier is added, as shown in Figure 75. In general, commercial sulfur cements possess the following characteristics (54 per cent sulfur) :

Tensile strength	480- 648 psi
Flexural strength	1500-2000 psi
Thermal coef. of expansion	$31 \times 10^{-6}$ to $48 \times 10^{-6}$

Another important filler employed in hot melts of sulfur is diatomaceous earth. Combinations of sulfur and powdered sand are recommended for

withstanding various hydrocarbons. These cements must not, of course, be exposed to open flames, as they are inflammable.

**Magnesium Oxychloride Cements.** The proportion of magnesium oxide and magnesium chloride is quite important. The cements prepared from these materials form hard, durable materials and are cold setting<sup>7</sup>. In one preparation, the following ingredients are dry mixed in the following proportions<sup>8</sup>:

	parts
Magnesium oxide	40
Barium sulfate	40
Chalk	20

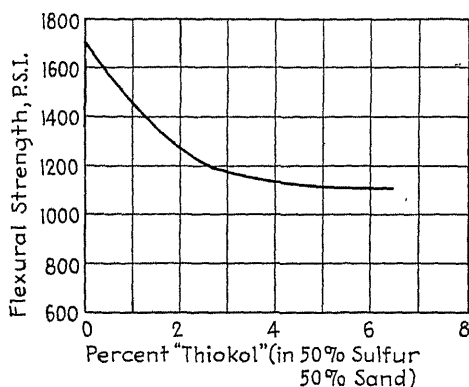


Figure 75. Influence of "Thiokol" on flexural strength (Duecker).

Then this is mixed with a liquid preparation comprising:

		parts
Magnesium chloride	27°Be solution	60
Hydrochloric acid	21°Be "	20
Sulfuric acid	22°Be "	20

The various magnesium oxychloride cements are mixed with water to the correct consistency and employed as an ingredient in a plastic composition or else as a cold setting plastic itself, capable of being pressed to various shapes for tools, patterns, jigs, and decorative articles. Various fillers such as powdered silica can be added to give sufficient body and minimize cracking tendencies. It is important to maintain closely controlled proportions of magnesium oxide and magnesium chloride.

Clarke has listed various trial formulas for magnesium oxychloride cement products<sup>8a</sup>. The dry mixes shown below are mixed with 22° Baumé solution of magnesium chloride. Typical formulas shown included:

	Percent by Weight		
	Casting Stone	Mixes Marble	Molding Mix
Magnesia	20%	20%	25%
Powdered Silica	25%		
Ottawa Silica Stucco Sand	50%		
Marble Flour		75%	60%
Powdered Talc			10%
Pigment	5%	5%	5%

**Litharge-Glycerol.** Cementing agents from glycerol-litharge combinations have been known for many years and are widely employed in the uniting of various conduits, providing a strong permanent bond. For ammonia gas, hydrocarbons, and corrosive solutions they have proven useful. In tests upon the efficacy of these cements, a proportion of 4 to 5 parts of litharge to 1 of glycerol has been recommended for pouring. This combination will set in two days, though higher temperatures and water will weaken the bond<sup>9</sup>. Stager also studied the mechanism of the setting of these cements<sup>10</sup>. In preparing waterproof tanks involving glass to metal seals, a typical cementing agent would be made from the following:

Litharge (PbO)	260 grams
Glycerine solution (2 parts: 1 part of water)	100 cc.

This is ground in a mortar and after a while is handled as a putty. It will harden in about one day and will make a good waterproof seal. Fine sand could also be added, as well as iron oxide to retard setting and prevent cracking. The litharge-glycerol cement is mixed freshly before each job, as it will not keep indefinitely. Ethylene glycol has also been substituted for the glycerol with some success<sup>4</sup>. Very little other work in this direction with organic compounds has been reported.

**Plaster of Paris.** Cements based upon plaster of Paris may be found every so often, inasmuch as the plaster is most easily handled and set with water. Two alternatives are possible: apply plaster directly and depend upon the chemical reaction with water to form a sound, substantial bond, or else combine plaster with other ingredients to accomplish cementing qualities. Plaster which has been set and chemically combined with water, is relatively porous and may be readily impregnated with synthetic resins to attain the desired degree of chemical resistance<sup>11</sup>. In fact the bonding qualities of plaster are enhanced after the proper impregnation procedure. Plaster is easily handled and low in cost, and is considerably improved through combination with plastic materials, in particular, low viscosity furane resins. Dry mixes of dimethylolurea or melamine formaldehyde with calcium sulfate hemihydrate (plaster) may

be added to water to obtain pastes suitable for cementing and sealing purposes. They are much more effective than plaster by itself.

In examining some formulations involving plaster, Moore<sup>2</sup> cited the following, which was recommended for fixing glass or stoneware or fused silica tubes into metal sockets:

	parts
Plaster of Paris	75
Kaolin	5
Lead fluosilicate	10
Lead oxide	8
Water to a paste	

Bennett<sup>8</sup> cited an iron cement prepared from the following combination

	parts
Powdered iron	72
Plaster of Paris	10
Gum arabic	8
Whiting	8
Sal ammoniac	2

Plaster cements have also been employed for flameproof enclosures of electrical apparatus<sup>12</sup>. Other noteworthy high strength gypsum cements include "hydrostone" and "hydrocal," which require much less water to make a mixture of pourable consistency. Considerably stronger end products are obtained which have negligible expansion during setting. Setting times may be controlled by small percentages of inorganic salts, such as sodium chloride and potassium sulfate.

**Miscellaneous.** There are various other cementing agents which have been employed in the bonding of chemical stoneware. Some of these have relied upon various drying oils while others have employed high polymers. Generally these cementing agents are relatively less porous than previous types which have been cited because the percentage of volatile material is held to a minimum. Graham and Catlow developed an adhesive for tiles, bricks, and wood blocks with whiting, barium sulfate, starch, and boiled linseed oil<sup>12</sup>.

For resisting acids, water, and steam, boiled linseed oil has been recommended for combination with china clay, powdered silica, unvulcanized rubber, melted pitch, and other constituents<sup>2</sup>. Resistance to sulfuric and hydrochloric acid is not as good as with other cementing agents. An expansion joint filler has been prepared from the following ingredients<sup>14</sup>:

	parts
Cottonseed oil	8
Linseed oil	8
Sulfur	8
Rosin	4
Silica	4
Blown asphalt	1

As a general laboratory cement for gas-tight joints and miscellaneous assemblies, Jackson recommends the following<sup>15</sup>:

	parts
Asphalt	1
Rosin	6
Rubber	3
Turpentine	1

The rubber is dissolved by the melted asphalt and rosin at a low temperature for 2 or 3 hours, followed by the addition of the turpentine. A pliable cementing agent is formed, which can be conveniently cast into sticks.

A non-hardening tile and glass cement has been developed from various non-drying oils and waxes<sup>16</sup>:

	parts
Tallow	340
Mineral oils	50-100
Aluminum oleate	50-100
Rosin oil	50-100
Powdered soapstone	400-1000

Various putties may be prepared for sealing joints in chemical stoneware. The following composition is effective for hydrochloric acid:

	%
China clay	54
Dehydrated tar	38
Anthracene oil	2.7
Asbestos wool	5.3

An asbestos putty for resisting cold nitric acid is prepared from powders and flock asbestos, china clay, and boiled linseed oil<sup>8</sup> (page 28), while litharge may be used for nitric acid strengths up to 56 per cent. This cement however requires several days for setting at room temperature. Coumarone resins may be developed in cementing agents for caulking purposes. They are readily melted, and can be combined with numerous fillers and modifiers to develop useful properties<sup>17</sup>:

	parts
Coumarone-indene resin (m.p. 50-60°)	60
Asbestos fiber	20
Iron oxide	5
Xylol	15
Pigment	5

The above composition may be troweled into position. Yamasita found that a vitreous envelope impregnated with synthetic resin behaved well at low temperatures as well as high temperatures, the resin insuring low temperature resistance and seal<sup>18</sup>. This has been employed as basing

cement for lamps. In sealing metallic members and ceramics, a composition produced from a blending of styrene and rubber has proven effective<sup>19</sup>. The styrene is hardened by polymerization *in situ*. This technique is, however, somewhat slow.

Furfuryl alcohol polymers alone and in combination with polyvinyl butyral have been employed in pickling tanks with considerable success<sup>20</sup>. Such a cement is excellent in the construction of corrosion-proof tank linings, floors and the like. These have also been applied as coatings for steel, cast iron, and concrete. Various inert fillers may be added to these cement compositions. The furane resin cements will resist most acids and alkalis up to high temperatures<sup>21</sup>. Considerable use is being made of furane resin cements in chemical stoneware, as they are much less porous than inorganic types.

### Bonds for Mica Plate

The cementing of thin flakes of mica plates into larger pieces is of the utmost importance to the electrical industry. There was a time when mica sheets were large enough and abundant enough to provide adequate high temperature electrical insulation as employed in the manufacture of electric flat-irons, heat units, toasters, etc. The growing scarcity of new sources of supply have made it imperative that the smaller sheets or splints be consolidated into larger integral units. The temperature resistance of mica is far above that of the organic high polymers, and at best most of the organic plastics can only serve as a temporary binding agent, holding the mica splints together as the electrical resistance wires are wrapped around them and as the assemblies are installed into their permanent position. Subsequent heating will decompose some of the resins, causing the units to "smoke" and eliminate volatiles. Shellac was one of the first temporary bonding mediums for this purpose, although polyvinyl esters and alkyds in solution have also been employed<sup>22</sup>.

High temperature resistance mica plates are manufactured at greater cost, using inorganic binding agents. Boughton and Mansfield used boric oxides and  $\text{H}_2\text{SiF}_6$ , fusing the constituents *in situ* to produce a bond between the mica splints<sup>23</sup>. A smaller amount of hydrofluoric acid was also employed for certain conditions.

### Cementing to Glass

The cementing of glass is of importance to the assembly of glassware or glass bricks, the development of optical goods, and the manufacture of safety glass. Various resins have shown much promise in this connection and the applications relating to this particular problem are varied. Generally in the laboratory, glassware components are fused to one another by

hot melting techniques, although certain materials have been developed for specifically bonding them. A paste of cupric oxide and phosphoric acid has been recommended as very satisfactory<sup>24</sup>. Ethyl silicate has been recognized as a useful adjunct in the bonding of glass bricks<sup>25,26</sup>. It has been recommended for addition to polyvinyl acetate adhesives and to nitrocellulose adhesives; its chemical relationship to glass no doubt makes it a valuable constituent. Ethyl silicate deposits silica on hydrolysis, making it a useful preservative for brick, concrete, and plaster. Mixed with siliceous powders, ethyl silicate forms weatherproof, acid-proof mortars and cements resistant to heat and chemical fumes. It affords a useful way of introducing silicate groupings into high polymer adhesives. It is quite probable that the silicone resin polymers will provide in the course of time a number of useful products for bonding glass and ceramic products. Many of the oils prepared from silicone resins have a pronounced wetting action upon glass surfaces—so pronounced that it is difficult to clean laboratory glassware. However, they will develop excellent moisture barriers for ceramics products, and are being used for this purpose.

Optical cements require good adhesives which are not embrittled by temperature extremes and which do not have pronounced cold flow, and are transparent. A naturally occurring resin, Canadian balsam, has long been used for much of this work although more recent resins show considerable promise. Davis and Wayman reviewed the adaptation of *n*-butyl methacrylate and an allyl type of resin ("CR-39") to the cementing of optical instruments<sup>27</sup>. The acrylic resin monomer is reacted with benzoyl peroxide at low temperatures and the reaction allowed to take place slowly until the polymer forms. Better results than Canadian balsam were reported. A hydrogenated wood rosin ester ("Staybelite No. 10") was also reported as an excellent plasticizer for butyl methacrylate. The writer has observed that hydro-abietyl alcohol makes an excellent light-colored plasticizer for butyl methacrylate and is of value in application as an optical cement. Another acrylic which has shown promise in precision optics is polycyclohexyl methacrylate<sup>27a</sup>.

There is considerable interest in various polyester resins as cements for glass. It has been observed, more as a matter of accident, that in preparing low pressure laminates against the face of a plate glass—presumably to obtain a smooth, glossy finish—the allyl type and the polyester resins such as "CR-39" and "Laminac" tend to stick so severely that chunks or pieces of glass are pulled from the surface. These resins have been approved for small and large lenses and prisms. They represent an important contribution to cold resistant optical cements<sup>28</sup>.

In the development of optical cements it is frequently necessary to

adjust the index of refraction of the transparent bonding medium to the glass lenses. This is often possible through different combinations of the transparent resins with their plasticizers. Folkoff, for example, explored the variation of the index of refraction of diethylene glycol diacetate and pentaerythritol-tetra-acetate combinations for optical adhesives<sup>29</sup>.

**Safety Glass.** The development of safety glass entails a specific problem in which a transparent sheet of organic plastic is secured to the surfaces of plate glass. Many of the transparent plastics have been prepared into assemblies of this nature, as outlined in earlier chapters on thermoplastic adhesive materials. Sheets such as cellulose nitrate and cellulose acetate required the application of auxiliary adhesives to secure a strong, durable bond to plate glass, whereas plasticized polyvinyl butyral resins which replaced them relied largely upon the specific adhesion they possessed for glass surfaces. Advantages of the polyvinyl butyral far outweighed other types. The adhesion is not of sufficient magnitude to cause a fracture of the glass if pulled apart in delamination, but nevertheless sufficient to maintain a strong, tight seal which precludes the admittance of air. Specific examples of the manufacture of safety glass which include discussions of the bonding of plastics sheets to glass are described in the following patent and literature citations:

- Cellulose nitrate in safety glass<sup>30</sup>
- Cellulose acetate in safety glass<sup>31</sup>
- Polymethyl methacrylate in safety glass<sup>32</sup>
- Polyvinyl butyral in safety glass<sup>33</sup>
- Polyisobutylene in safety glass<sup>34</sup>

Among other glass adhesion problems which have arisen in recent years is the development of means of protecting glass against scattering after the shattering effects of high explosives. This problem is kindred to the requirements of thin glass shells employed in the manufacture of flashlight bulbs employed for photographic purposes. In both instances a high pressure gradient is sufficient to fracture the glass and send it flying, unless it can be mechanically restrained. One way of accomplishing this is through the use of thin films of strongly adherent polymers which will hold the fragments of glass. Polyvinyl acetate is one which has been employed. Among other approved methods of protection are adhesive tapes criss-crossed across the window-pane, or special laminated constructions reinforced by wires<sup>29</sup>.

### Bonding of Abrasive Particles

Most adhesive materials have at one time or other found their way into the bonding of abrasive granules—either in the manufacture of grinding

wheels or else in the manufacture of flexible, abrasive papers. There were numerous examples cited in earlier chapters of specific applications of binding agents to the manufacture of grinding wheels and the like; at this time, the subject will be reviewed collectively and the specific problem of adhesion to the abrasive grains examined. The requirements of a bond for abrasive particles are many—strength is of the utmost importance, inasmuch as when the abrasive grains do their work, there is a pronounced tendency to shear them from the binding medium. For most efficient abrasive action, the proportion of abrasive particles should be high and the percentage of bonding medium relatively small. Where the manufacture of sandpapers or abrasive papers are involved, only one side of the abrasive grains are adhered to the flexible backing medium, the other must be exposed for the abrasive work. On the other hand, in the manufacture of grinding wheels the abrasive grains are completely imbedded, and they make their appearance as the wheel wears down in the course of its work. “Resinoid” bonded wheels have long been standard for special grinding and cut-off operations upon metal stocks.

The alignment of abrasive particles upon a cloth or paper backing requires considerable skill in order to achieve the maximum in cutting efficiency. In one process, the position of the abrasive particles is changed by subjecting them to the action of an electrical field. The mechanical features of the apparatus for preparing these abrasive cloths are described in detail by Schacht<sup>36</sup>.

A review of early applications of synthetic resins to sandpaper and emery paper was given by Carlton<sup>37</sup>. One of the earliest problems in the manufacture of grinding wheels was the adequate wetting of the surface of the abrasive grains. Hartmann and Easter suggested sodium fluoride for this purpose, which rendered the glue more fluent when applied<sup>38</sup>. They pointed out that adhesion between the solids is greatly increased when the solid surfaces are treated with an agent which increases surface tension or fluidity of adhesive in a liquid state—but which does not have a deleterious action when “set” or solidified. On the other hand, furfuraldehyde has long been used, aiding the utilization of phenolic resins in the manufacture of grinding wheels.

**Abrasive Papers.** Oxidized linseed oil plus 4 per cent of asphalt has been used as a waterproof binding agent for abrasive cloth or paper<sup>39</sup>. Cellulosic derivatives have long served as binders for abrasive grinding wheels<sup>40</sup>. Various abrasive agents can be added to improve the flexibility. In general there are two types of sandpaper—wet and dry—or special papers used for both purposes. Many sanding operations are done solely by dry sanding—woodwork for example. On the other hand, in the sanding of phenolic or acrylic sheets, as in the fabrication of these materials, a

wet sanding may be preferred to carry away the dust and particles removed from the surface. Wet sanding is less dusty than dry sanding, and there is less chance of overheating the work. Oglesby has done considerable work in the application of abrasive particles to paper or fabric. He has shown a preference for synthetic resins in some applications<sup>41</sup>. Alkyd resins have long served in the manufacture of sandpaper, generally with the addition of a non-drying oil as a flexibilizing agent<sup>42</sup>. Oil modified phenolic resins which are even more important, have also been employed as well as alkyds for application to abrasive papers<sup>43</sup>. In view of the greater flexibility of the oil modified types of thermosetting materials, these certainly are to be preferred to the more rigid thermosetting compounds in the manufacture of flexible abrasive papers or cloths. While a phenolic resin may for example be employed as a binder for the abrasives, the relatively porous backing may be treated with a material such as olefin polysulfide<sup>44</sup> or other agents.

Of course, the inorganics such as sodium silicate may also be used for bonding the grit to a flexible backing material<sup>45</sup>, although the trend is toward more recently developed synthetic resins such as resorcinol-formaldehyde<sup>46</sup>. The construction of abrasive papers is not simple by any means—generally consisting of the addition of several essential elements such as<sup>47</sup>: (1) sheet backing material; (2) sizing coat of synthetic resins—a waterproof adhesive such as polyvinyl acetal or cellulose derivative; (3) a water resistant grit bonding agent, which is less flexible and heat hardenable; (4) abrasive grain deposit.

Netherly bonded abrasive grains with polymerized monohydric alcohol esters of alkyl-substituted acrylic acid<sup>48</sup>. Not only is the adhesion problem in the manufacture of abrasive papers and cloth a difficult one, but also the assembly. Oglesby added abrasive grains to an adhesively coated sheet in an atmosphere charged with vapor of solvent for adhesive<sup>48a</sup>. Adhesion has also been aided through application of high frequency field for curing the abrasive grains in position<sup>48b</sup>.

There are various methods for the attachment of abrasive belts or discs to sanding machines. When they are formed as a continuous loop, there is the difficult problem of scarfing them together and joining one end to another—usually accomplished by the manufacturer of the abrasive belt. These belts or loops are rotated by motor driven drums or rolls, and in operation pass in close proximity to a flat surface which serves as a backing plate, when pressure is applied from the object being sanded. Discs or abrasive paper are also cemented by some tacky thermoplastic adhesive to a rotating steel disc directly attached to the end of a motor shaft or driven by some pulley.

In other miscellaneous applications of bonding agents to abrasive cloth or paper, polystyrene<sup>49</sup>, cyclized rubbers<sup>50</sup>, emulsified asphalts<sup>51</sup>, and urea

alkyd combinations<sup>52</sup> have been proposed. The importance of animal glues in low cost sandpaper manufacture, should not be overlooked, however.

**Resin-bonded Wheels.** While the great bulk of grinding wheels are bonded with inorganic agents, a large number of specialty grinding wheels for cut-off and other purposes, are manufactured from phenolic resin bonded grains. Abrasive particles are of different grit size, depending upon the function to be performed, and usually prepared from silicon carbide and aluminum oxide ( $\text{Al}_2\text{O}_3$ ), although boron carbide is coming into greater prominence. Emery is also used, but its cutting power is less satisfactory than the others previously cited, which are high up on the scale of Moh's hardness. There are many fundamental factors which determine the behavior of grinding wheels. Temperature resistance is quite important, as the temperature rise is quite severe following pronounced cutting down or grinding. Consequently the thermosetting resins have been featured in proposed constructions for grinding wheels.

The manufacturers of grinding wheels are quite alert to new resin possibilities and the patent literature is replete with various combinations of synthetic resins with abrasive grains. To examine a few of these proposed combinations we shall take a few examples at random, such as the polyesters<sup>53,64</sup>. The number of allyl-type and polyester resins is quite large, and no doubt some types will prove to be more acceptable than others; however, an organized study of the behavior of this resin type with abrasives has not been published. There will always be new ways of using and developing the optimum properties in the older resin binders. Alkali treated phenolics have been proposed<sup>54</sup>. Sanford described various methods of manufacturing grinding wheels under heat and pressure<sup>55</sup>. To Baekeland however, goes credit for first pointing out the advantages of the phenolic resin bond for abrasives<sup>56</sup>, though the first marked improvement was the introduction of 3 to 4 per cent of furfuraldehyde to the abrasive particles before incorporating the phenolic resin binder<sup>57</sup>. The presence of furfuraldehyde, it will be remembered, assisted the flow of the phenolic resin, when molding and shaping the grinding wheels under pressure.

In further proposed applications of plastics in the manufacture of grinding wheels we can examine the work of Kistler, who has investigated the employment of urea, melamine, and aniline formaldehyde resins as binders<sup>58</sup>. Berger's work in this direction may also be noted<sup>59</sup>. Swain and Light combined phenolics and melamines in the manufacture of experimental grinding wheels<sup>60</sup>. While thermoplastics have not proven as satisfactory as the thermosetting materials, the patent literature does record a few examples. Robie employed polyvinyl acetals<sup>61</sup> and acrylic acid esters<sup>62</sup> for this purpose. Nimwegen used chloroprene polymers successfully<sup>63</sup>. It may also be noted that rubber-bonded abrasive grinding discs and wheels

of relatively small dimensions are widely used on small portable grinding tools. While they wear rather rapidly, they have proven invaluable in tool manufacture, as a grinding medium for reaching into small openings and performing a cutting down operation. Coes showed preference for aminated phenolic resins, with cross-linking agents which will react at the amino groups, as binders for abrasives<sup>65</sup>. Smith found the addition of zein to the phenolic resin wetted abrasive particles to be helpful during molding of the abrasive articles<sup>66</sup>. For higher grinding speeds, organo-silicon resin binders have been specified. Possessing higher temperature resistance than other plastics, this series of resins would be outstanding in grinding wheel applications, though costs are still prohibitive<sup>67</sup>.

In these and other ways the high polymers have been combined with inorganic products. Unusual problems arise from a heat and abrasive standpoint, but wide scale applications of resin bonded wheels point to their efficacy.

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## Chapter 20

### Tests and Specifications for Adhesives

Tests and specifications for adhesives are as numerous as there are applications for adhesives. Nevertheless within recent years there has been a more organized and coordinated effort to reduce the problems of adhesion to basic methods of evaluation, as an aid to furthering research by providing a common meeting ground which would enable one laboratory to compare results with another. During 1944, for example, committee D-14 was organized by the American Society for Testing Materials to establish test methods for animal, vegetable, synthetic, and mineral adhesives<sup>1</sup>.

During the war numerous process and material specifications were established by the armed forces to assist in the development of adhesives for their particular requirements. Much of the discussion on testing methods will draw rather liberally from these specifications which were developed at Wright Field, Forest Products Laboratory, Naval Aircraft Factory, and the Bureau of Standards. The majority of the specifications were however directed towards the bonding of wood, and while a few made recommendations for the bonding of metal parts, much work remains to be done before universal agreement is forthcoming on the most satisfactory procedures in that field. It is hoped that further encouragement will be given to these efforts at standardization, inasmuch as adhesives have been applied by trial and error methods, with too little examination of the fundamentals of the bonding agents and their probable behavior under some specified conditions. The use and application of adhesives are arts in themselves and likely to be unsatisfactory in unskilled hands, because the best adhesives prepared are worthless in the hands of those failing to observe precautions well established by field and laboratory tests.

The great majority of adhesive applications, whether they be two pieces of metal cemented together or the cover flap of a paper envelope, require a permanent bond resulting in some failure of the surface being bonded before failure of the adhesive. The adhesive can only then be said to be stronger than the material it bonds—an ideal condition. On the other hand, temporary bonds as with pressure-sensitive tapes have their merits in special cases. There are various ways of testing a cemented assembly to destruction, involving either shear, tension, or a combination of both. On the following pages some of the highlights of important testing methods are reviewed for reference purposes.

### Tests for Wood Adhesives

There have been more specifications developed for the testing and evaluating of wood adhesives than for any other material dependent upon bonding operations for assembly. These specifications are particularly concerned with the properties of the end product, though in recent years more attention has been given to characteristics of the adhesives; however, in all cases these characteristics are considered secondary to the end results attained. Inasmuch as the properties developed in the assembled wood components are of paramount interest, the conditions of application will naturally have some bearing upon the specifications, and the interpretation

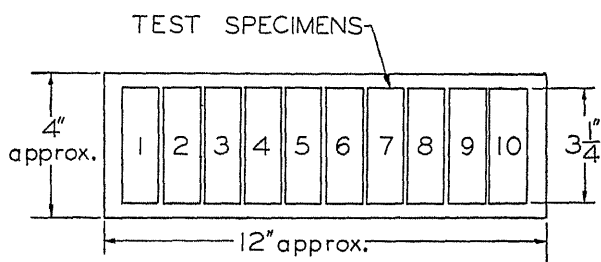
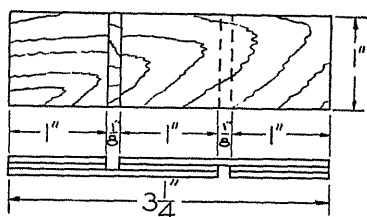


Figure 76. Plywood strip shear samples cut from above panel.



PLYWOOD GLUE SHEAR-TEST SPECIMEN

Figure 77

of water resistance, for example, is determined by whether outside or inside weather exposure conditions are encountered. The following list of specifications are by no means complete, though they represent those specifications most widely used and are indicative of prevailing test methods.

*Army-Navy Aeronautical Specification, AN-NN-P-511b, Plywood and Veneers, Aircraft Flat Panel (superseded by AN-P-6, same scope).* In this test specification flat pressed plywood panels are subjected to strip shear tests. Specimens are selected from plywood panels as in Figure 76 and then cut to size as in Figure 77. When the face plies are 0.047 inch thick and smaller, the spacing between saw slots is  $1\frac{1}{2}$  inch. The saw cut is approximately  $\frac{2}{3}$  through the center core. A special pair of tension grips

for holding test specimens is shown in this specification, though the wedge-shaped jaws of the universal testing machine generally prove satisfactory for most requirements. While true shear is not developed (because of bending taking place in the test specimen during loading, due to the presence of some tension as well as shear stresses) this specification has proven valuable for testing the quality of aircraft plywood samples.

For comparative tests upon adhesives, glue manufacturers generally employ vertical grain birch, 1/6 inch veneers, or in some cases maple veneers of the same thickness. Shear strengths of the order of 500 to 550 psi are obtained upon the best adhesives, failure usually occurring in the wood—thus preventing a true determination of the shear strength of the glue. This specification defines minimum values for a number of species of aircraft plywood and contains numerous details for selecting correct veneers and eliminating wood defects. In addition to dry strip shear tests, the aircraft plywood test samples are machined and placed in boiling water for a period of 3 hours and then cooled in cold water and tested while wet. Shear strength values for veneers such as birch and maple must exceed 300 psi when tested wet. Animal, vegetable, urea, and protein adhesives have difficulty in meeting this latter requirement; they tend to delaminate even before test or fail at very low loads. The adhesives usually meeting this specification are melamine, melamine-urea resins, phenolics, and resorcinol-formaldehyde resins.

*Army-Navy Aeronautical Specification, AN-G-8 Glue, Cold Setting Resin.* This specification is intended to cover the use and application of cold setting adhesives in assembly or secondary bonding operations. The forms of the adhesive are described; both powdered and liquid types are permitted, usually with separate catalysts. A working life of 2 to 8 hours is generally provided for, and the maximum amount of filler permitted is 20 per cent. The AN-strip shear test described in the previous specification, is performed upon a plywood panel, prepared from 1/16 inch birch. Another important test procedure is the block shear test, details of which are illustrated in the accompanying sketches (Figures 78, 79). As the load is developed the shear appears along the single glue line. Maple blocks are selected for grain and carefully prepared with 20 to 25 grams per square foot of glue spread on one surface, then put under a pressure of 200 to 250 psi for 8 to 24 hours at 75 to 85°F. They are conditioned for at least 6 more days before the test. Shear strengths in excess of 2800 psi should be exhibited by these test specimens.

This specification also has a provision for the control of glue line acidity, which shall not be less than a pH of 2.5. This is determined by spreading out a film of glue and allowing it to air dry for 12 to 15 hours. After this it

is ground and placed in contact with distilled water, and the pH is read at specified intervals. This specification is readily met by a number of urea, resorcinol, and furane resin adhesives. Some of the phenolic cold setting adhesives are on the borderline because of their high acidity.

*Army-Navy Aeronautical Specifications, A N-P-43, Plywood, Aircraft Molded.* This specification governs primary bonding operations for aircraft plywood, permitting only the use of thermosetting synthetic phenolic and urea resins—usually hot pressed types. Sample flat panels may be prepared and wet and dry strip shear tests performed as in AN-NN-P-511 specification previously described. A test at the option of the aircraft inspector may require soaking in water at room temperature for 48 hours and drying for 8 hours, no delamination being shown either wet or dry. Edge gluing and scarfing procedures are carefully controlled and completed

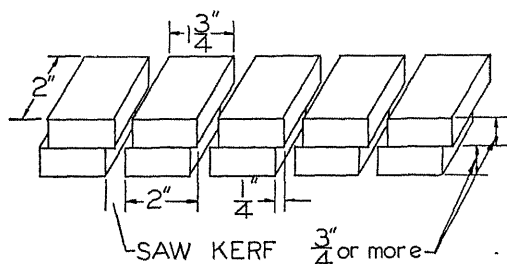


Figure 78. Samples for block shear test.

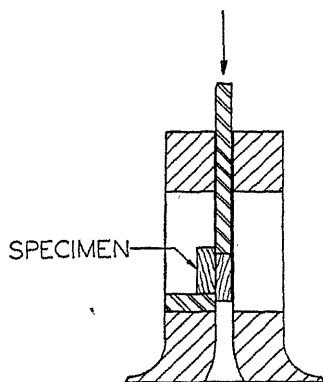


Figure 79. Method of applying load for block shear test.

with water resistant adhesives. Another characteristic of glues employed in bag molding, which is of general interest, is their slipping tendencies when placed under heat and pressure. This indicates how readily the plies would adjust themselves during the molding operations. A Forest Products Laboratory report outlines one testing procedure for the slipping characteristics at molding temperatures, employing an assembly about a steel 2 inch diameter mandrel and measuring the force required to cause slipping<sup>2</sup>.

*Ministry of Aircraft Production (England) D.T.D. 484, Cold Setting Resin Glue (Gap-filling).* This specification is of particular interest because it makes provision for tests of resin glues where thick gaps may be involved. Powdered or liquid cold setting adhesives are admitted. In this test 1/8 inch European beech veneers of selected straight grain are bonded together on a simple lap joint of one inch and a similar test specimen with 0.050 inch

gap joint formed by the insertion of an 0.050 inch veneer. The minimum average test loads shall be as follows :

Dry test—Not less than 600 pounds

Wet test—Not less than 450 pounds

Gap test—Not less than 450 pounds

*Ministry of Aircraft Production (England) D.T.D. 335, Cold Setting Resin Glue (Non-gap Filling).* Glues complying with this specification must be used only in those joints where the whole of the surfaces to be joined can be brought into close contact by means of adequate pressure, and where gaps in the glue line can be avoided with certainty. In the wet test, samples are immersed in water for 6 hours at room temperature and then tested while wet. They are conditioned for at least 6 days at 25°.

*Army Air Forces Specification, AAF 14124, Glue, Low Temperature Setting Phenol, Melamine, and Resorcinol Base.* This specification was prepared after some of the newer melamine and resorcinol adhesives had made their appearance. The liquid and powdered adhesives are recognized, with a minimum storage life of 30 days for the liquid adhesives. The pH of the glue line film was set at a value above pH of 2.5. In addition to boiling water tests, soaking tests for 48 hours at room temperature are specified and the strength of the glue evaluated by wet strip shear tests. Test values are the same as in ANG-8 and AN-NN-P-511.

**Weather Exposure Tests.** While the standard government specifications have not given in great detail the procedures for conducting weather exposure tests, reports from the Forest Products Laboratory, covering a period of four years in some cases, have been most helpful in making known the results of weather tests or their laboratory equivalents. These tests entail combinations of wet and dry exposures, followed by physical tests such as strip shear or block shear upon the cemented assemblies. A summary of information on the durability of aircraft glues was reported by Wangaard<sup>3</sup>. These studies have provided the basis for recommendations on the fabrication and assembly of wood aircraft and their accessories. Among the various cycles employed for the evaluation of wood adhesives were the following :

(1) Continuous soaking in water at room temperature : This test determines water resistance.

(2) Continuous exposure to 97 per cent relative humidity and 80°F : In this test, resistance to mold and other microorganisms is measured, as well as the ability to withstand the effects of moisture content approaching the fiber saturation point. In some earlier government specifications a mold culture was developed from potatoes under conditions of high humidity and in intimate contact with the plywood<sup>4</sup>.

(3) High and low relative humidity cycles : A period of two weeks at 80°F

and 97 per cent relative humidity is alternated with a 2 week period at 80°F and 30 per cent relative humidity. Mold growths, resistance to water, and strength factors are periodically measured.

(4) Soaking-drying cycles: Repeated cycles of alternate soaking in water at room temperature for 2 days and drying at 80°F and 30 per cent relative humidity for 12 days are followed.

(5) Continuous exposures at one of the following: 80°F and 65 per cent relative humidity; 158°F and 20 per cent relative humidity; or 158°F and 60 per cent relative humidity.

(6) Room temperature—high temperature cycle: Repeated exposures for 16 hours at 80°F and 65 per cent relative humidity and 8 hours at 158°F and 20 per cent relative humidity measure the effect of high temperature and moderate to low moisture content.

(7) Room temperature—low temperature cycle: Sixteen hours at 80°F and 65 per cent relative humidity and 8 hours at -67°F over dry ice determine the effect of very low temperatures upon the glue line.

Some of the data observed in these tests were indicated in the chapter on wood adhesives, and they emphasize the superiority of the phenolic and melamine adhesives, followed in turn by the urea resins, then water resistant casein types, and the animal and vegetable glues. High and low humidities adversely affect casein glues without preservatives<sup>3</sup>.

Not all laboratories are equipped with facilities for running high-low humidity cycles, and one of the most popular methods of test is the soak-drying cycles. These tests have been performed upon laminated lumber. Severe stresses may be developed in the test specimens, and in one of the commercial test methods a 12 inch diameter, two-ply laminate with cross-grained layers (3/4 inch thick) is immersed in water for 48 hours and dried. Not more than 1/12 of the periphery shall exhibit evidence of delamination. Other standards for Douglas fir-plywood follow cycles of 48 hours of soaking in water and 8 hours of drying at 145°F<sup>5</sup>. High percentage of wood failure is looked for after shear tests are performed.

Need for more data on the effect of moisture cycles upon the performance of wood adhesives was never more pressing when during World War II, shipping crates of plywood delaminated on reaching South Pacific islands. These occurrences lead to greater utilization of the synthetic resin types. With greater interest in structural adhesives, the building codes of various major cities are being revised to include test conditions and methods of evaluating laminated timbers for building purposes<sup>6</sup>.

In evaluation of wood adhesives, both room temperature and boiling water tests represent methods applicable to wood glues. Boiling water tests alone may not be acceptable because they may cause the thermosetting synthetic resin glues to polymerize further; hence the need for low tempera-

ture performance. The phenolic resin types and furane resin types are the best from the standpoint of resistance to cold and hot water. The water resistant tests and the cycles of high and low humidity are even more more marked in effect when the glue lines are relatively thick and when, as in the case for the majority of solvent type adhesives, crazing and cracking occur in the glue.

**Vibration and Creep Tests.** The data for vibration and creep tests are still fairly limited when compared to other properties which have been evaluated. Dietz and Grinsfelder conducted fatigue tests upon urea and phenolic resin adhesives, and presented some useful information<sup>7</sup>. Adhesives are frequently subject to vibrating loads which induce alternating stresses in the glue. Shear in the plane of the glue and direct tension perpendicular to the glue line are the two most likely to bring about failure. In one series of tests upon cold setting urea adhesives, test specimens of 1/8 inch rotary cut maple veneers were made up with an overlap of 1½ inches. The centers of the specimen were forced back and forth by a pusher, connected to a driving rod operating off an eccentric. The speed of oscillation was established at 1100 to 1300 rpm in this special machine<sup>7</sup>. Wood fatigue as well as rupture in the glue line occurred under the conditions of test, though when maximum tensile stresses were below 120 psi the specimens did not fail. This is determined from extrapolation of the fatigue curves.

In another group of tests the fatigue behavior of wood laminated with phenolic resins, and the effects of weathering and high and low temperatures were determined<sup>8</sup>. Cantilever type fatigue machines were employed operating at 1100 to 1300 rpm. The eccentric was adjustable to give a throw up to 1½ inches. Fatigue failures proved to be primarily wood failures. While weathering did not affect the phenolic adhesives, low temperatures showed a marked loss in glue line shear strength.

Much further data remains to be performed before a good picture of fatigue strength of the adhesives can be determined. One of the most important factors will probably be the glue line thickness, with a more rapid fall off in strength appearing as the gap becomes greater. The somewhat porous nature of most adhesives of the solvent type will be reflected in low fatigue strength under oscillatory types of stresses. Simultaneous exposure to high and low humidities under vibration will also prove revealing and rapid loss in strength more apparent than under ideal temperature and humidity conditions.

Stresses induced in one direction to bring about the effects of creep are also enlightening. Plywood has been stressed as a simple cantilever beam and some data have been reported on creep characteristics<sup>9</sup>. Still another method is to prepare an assembly of two wood components in an overlapping relationship, and while one part is supported the other is loaded

as a simple cantilever beam. Most of the stress concentration appears upon the glue line, and creep takes place quite rapidly. Thermoplastic polymers will yield much more rapidly than adhesives based on the thermosetting derivatives. The effects of temperature on this creep rate are also marked. In these directions the physical properties of wood adhesives are most meager although work is in progress to eliminate gaps in engineering information.

**Miscellaneous Specifications on Wood Adhesives.** There are a few specifications for wood adhesives which have not entered into the discussion so far. Some of these are tabulated herewith:

(1) *AAF-15072, Plywood, Container.* Weatherproof construction requires a hot press phenolic, while protein glues will be admitted for moisture resistant types.

(2) *Federal Standard Stock Specification, NN-B-601 A, Boxes, Wood-Cleated Plywood.* Various grades of plywood are specified according to their degree of water resistance. Graduated soaking-drying cycles are specified for the various types.

(3) *Bureau of Ships, R-39-O-7, Oak, White, Laminated (Ship Use).*

(4) *Bureau of Ships, R-39-F-3, Fir, Douglas, Laminated.*

(5) *Bureau of Ships, 52-G-12, Glue, Phenol Formaldehyde, Low temperature Setting.* Block shear and plywood strip shear tests are specified.

(6) *Bureau of Ships, 52-G-11, Glue, Resin (Urea Formaldehyde).*

(7) *Ordnance Department, A XS-1102, Glue, Urea Formaldehyde Resin, Wood Cargo Boxes.*

(8) *Bureau of Supplies and Accounts, Navy, 52-G-8, Glue, Casein, Water Resistant.*

(9) *Federal Specifications, C-G-451, Glue (Animal) Wood Working.*

(10) *AAF-3-152-A, Glue, Casein (Water Resistant).*

**Interpretation and Evaluation of Wood Adhesives.** The various specifications which have appeared for wood adhesives have placed emphasis upon the qualities of the assemblies, rather than the characteristics of the glue itself. This is a rather liberal viewpoint, because it permits new glues which possess superior performance to find admission to important applications. Many of the physical tests devised for wood adhesives are adaptable to tests upon other materials. Nevertheless, there is some divergence of opinion regarding the best methods of conducting the tests. In some instances three block shear test specimens are preferred to the double block test specimen, although results have not been correlated. Then again, plywood strip shear tests and their results are closely related to how samples are held during the test, the type of machine for applying the load, and the rate of applying the load.

The pH of the glue line has been the subject of much discussion; it is

recognized that it may not necessarily be the wood which is affected, but the glue line itself which suffers adversely. The limit of pH has been arbitrarily established at 2.5 in the presence of water. Exposure of the glue film to the atmosphere in the conduct of this test may result in evaporation of volatiles which may contribute to a different pH than when enclosed between the surfaces to be bonded. Further, the hydrolysis of the water may prove to have extraneous effects upon the components present in the adhesive, particularly when non-water-soluble adhesives are employed.

A greater share of attention should be given to thick glue lines, which appear unavoidable in field assembly operations of wood adhesives. Among other characteristics which are of practical importance to manufacturers applying the adhesives are the following:

(1) Viscosity time curve for the adhesive after it has been activated and made ready for application. Strength characteristics at different intervals of the pot life would be helpful.

(2) Rate of developing strength under the curing conditions (whether they be at room or elevated temperature). Designate strengths suitable for handling the assemblies as well as maximum strengths possible after full cure of the adhesive film has been reached.

(3) Storage life versus viscosity of the adhesive. These data would indicate the useful life expectancy.

(4) Maximum permissible open assembly period for the glue film thickness when the recommended spread is applied to the surface. Strength characteristics after different open assembly times would be helpful under controlled thickness of glue line.

(5) Effect of moisture content of wood on the ultimate strength of the glue line.

(6) Relationship between shear strength and glue line thickness.

(7) Effect of cold and boiling water on strength characteristics.

(8) Strength properties at low and high temperatures. If the strength drops off quite rapidly with higher temperatures, the creep properties should also be evaluated.

(9) If two or more components are combined to prepare the adhesive, some data should also be given on the effect of variables in the relative proportions. The effect of different percentages of catalyst would also be helpful.

### Tests for Metal Adhesives

Adhesives for metal products are still in their infancy, though much attention was given to their formulation and evaluation during World War II. Vibration tests; high and low temperature tests; creep tests; shear, tension, and impact tests; and the effects of weathering are most important

for these adhesives which are used for structural purposes. In the chapter on metal and rubber adhesives, the influence of joint dimensions on physical properties was brought out.

*Army Air Forces Specification No. 20032, "Cementing Metal to Metal and Metal to Wood, Process For"*. The specification enters into considerable detail on the chemical processes for preparing metal surfaces for bonding. Elaborate treatments are outlined for cleaning steel, aluminum, and magnesium. Test specimens one inch wide are cut from a six inch wide panel and when cemented together measure  $7\frac{1}{2}$  inches over-all with a one-half inch overlap at the center. Alclad 24 ST aluminum alloy is usually specified in this test. The joint is loaded at a rate of 750 to 1000 pounds per minute, and tensile shear strength of at least 2500 psi must be exhibited. Metal-to-metal bonding is generally performed at 200 psi.

*Army Air Forces Specification No. 20034, "Cementing Metal to Metal, Process For"*. As in the previous specification elaborate cleaning procedures are recommended for the metal surfaces. After application, the cement is air dried thoroughly and then pressed at 280 to 300°F. Some manufacturers recommend a high temperature pre-curing operation which is quite important to obtaining a good shear strength in the test specimen. The specification reflects one or two proprietary cements currently approved for metal bonding, establishing procedures not adaptable to all types of metal cementing agents. For example, "metal cement that has not been shaken or stirred before using and at least once every two weeks while in storage shall not be used."

Metal and rubber adhesives have also been used for another special testing purpose, and while the test is designed for evaluating negative air loads on aircraft structures, it does necessitate strong and acceptable adhesives<sup>10</sup>. Patch areas are laid out upon the surface of the aircraft structure, to which are cemented a neoprene sponge pad which has been cemented to a metal or plastic base plate. Tension loads as high as 4000 pounds per square foot can be obtained on the sheet metal structure. The adhesive patch method is used principally for testing wing structures, canopies, radomes, doors and engine cowlings. Direct tension pulls are applied to simulate negative air loads.

A jet of water impinging at a 45° angle at the edge of an isolated area has been the basis of a test for adhesive coatings upon metals<sup>11</sup>. High speed rain abrasion tests have also been performed upon glass cloth laminates. Rubbery protective coatings at least .010" thick gave good protection<sup>21</sup>.

### Tests for Rubber Adhesives

Rubber to rubber assemblies and rubber to metal assemblies are generally the subject of rubber adhesive specifications. While many of the manu-

facturers have prepared their own specifications and procedures to be followed in applying adhesives a further degree of standardization appears desirable. Two standard physical tests have made their appearance, one involving a tensile shear between two metal strips with a rubber layer sandwiched between, and the other, written into an A.S.T.M. specification requires a tensile pull upon two surfaces of rubber or rubber-to-metal bond. Complete failure in the rubber is generally expected. While preparation of rubber surfaces by cyclization or at least by the application of a strongly adherent primer coating of chlorinated rubber or cyclized rubber has been a standard practice before the final bonding operation, the advent of a number of new synthetic rubbers leaves these techniques still in a state of flux. Simultaneous attachment of metal inserts at the time of vulcanization of the rubber is one typical problem, and the cold assembly of vulcanized rubber stocks represents another.

*ASTM. D-816 "Rubber Adhesives"*. These test methods are intended for use in testing the properties of adhesives manufactured from natural rubber, reclaimed rubber, synthetic elastomers or combinations. The tests are divided into two parts: (a) test for adhesive strength, bonding range, softening point and cold flow; and (b) determinations of viscosity, stability, cold brittleness, and plastic deformation. Various precautions are observed for applying the adhesive cementing agent. Two types of spreaders are employed, a volumetric cement spreader and a dead weight cement spreader. The adhesive strength is determined by:

- (1) Direct tension pull in direction normal to adhered surfaces (see ASTM D-429 below).
- (2) A shearing force in the same plane as the surfaces. Two type specimens are used: type I, a simple one inch overlap between 5 inch long non-extensible materials such as metal or leather; and type II, a sandwich specimen having an extensible 1/8 inch thick block cemented between two non-extensible strips.
- (3) A stripping force producing progressive separation over the adhered surfaces (see ASTM D-413 below).

In determining the softening point a one pound dead weight is hung upon each specimen (one inch wide) and temperature raised at a rate of 15°F for 20 minutes. Temperature at which bond fails indicates softening temperature. Cold flow under dead weights and for stated time intervals are observed.

*ASTM D-553 "Viscosity and Solids Content Tests of Rubber Cements"*. This test describes funnel viscosimeters and falling cylinder methods for viscosity measurements. Tests are made at  $25 \pm 2^\circ$  and precautions are taken against excessive solvent evaporation rate. For stability tests, specimens are kept at 60° and the changes in room temperature viscosity are

noted. Cold brittleness is examined by applying the rubber cements to 0.040 inch aluminum which is bent over a 3/8 diameter mandrel after low temperature exposures.

*ASTM D-429 "Adhesion of Vulcanized Rubber to Metal"*. A rubber cylinder vulcanized between and bonded to two metal plates is the test specimen in this specification. The jaws of the testing machine are separated at a rate of one inch per minute. The cylinder is 1.597 inches in diameter and 0.5 inch in thickness, and cemented to 3/8 inch thick metal plates of the same diameter (SAE No. 1020 steel).

*ASTM D-413 "Adhesive of Vulcanized Rubber (Friction Test)"*. These methods cover the procedures for testing adhesion strength between plies of fabric bonded to rubber or the adhesion of rubber layers to other materials. Dead weight and machine loading methods are described. The adhesion is expressed as: average force to cause separation at a definite rate or average rate of separation under a specified force. The separating layer is stripped from the specimen at an angle of 180°. Tests are also provided for measuring the force required to pull a single cord in the direction of its axis (known as "H" test). The force of adhesion has been shown to be dependent on gage of cord and contact length (22). Higher test results at elevated temperature are reported for natural over synthetic rubber.

Two chief bonding tests appeared for rubber products in Germany during World War II<sup>12</sup>. A small cylinder tubed or rolled from calandered stock is cut into two halves and cemented together. The assembly is vulcanized together. The cured cylinder is run to failure in a flexing machine under tension and compression. A cord adhesion test was devised for testing the adhesion of rubber cemented cords between two layers of Buna carcass stock. The ends of the cords protruded and after attaching 1 kg weights were oscillated to failure.

Werkenthin has described a number of adhesion tests for rubber products, which included the following (23):

a. *Strip and Shear Adhesion for Cements*.—This method has been used in evaluating battery compartment linings and is determined upon sheet rubber to sheet metal. A one-inch wide strip rubber is cut back and dead weights added until a separation of one inch per minute occurs.

b. *Uniform Rate Spring Scale Strip Adhesion Test*.—A test method was developed in which the line of load was applied at 90° to test panel at a rate of one inch per minute. The spring balance moved in the direction of the stripping so that a 90° angle was always applied.

c. *Hydrostatic Adhesion Test for Hollow Shaft Covering*.—For hard rubber stocks which cannot be folded back, a test method was developed in which hydrostatic pressure was applied to circular grooves until separation occurred.

d. *Shear and Tension Adhesion Tests*.—These tests employed either a

three plate yoke for true shear or a direct tension pull for evaluating the adhesive.

e. Machine Method for Strip Adhesion Test.—A one inch wide rubber strip is folded back and passed over a  $1\frac{3}{4}$  inch diameter cylinder.

### Tests of Adhesives for Plastics

Adhesives for organic plastics have generally been evaluated by methods established for wood testing, such as block shear and strip shear tests. These methods have not been fully acceptable, however, as they do not give a true picture of the specialized requirements of the organic high polymers. The thermoplastics which are generally welded by solvent cements or in special cases by heat welding may require examination of the visible joints if transparent, as air bubbles and the like may interfere with perfect clarity. However, structural assemblies of the thermoplastics have been limited. There are two important points to examine: the fit of the joints to be assembled and the rate at which strength is developed in the joint after the solvent cement has been applied. Well fitted thermoplastic parts will be welded together quite satisfactorily by solvents, and mechanical inspection of proposed assemblies should be a prerequisite for the cementing of thermoplastics.

The thermosetting plastics may be tested by two block or three block shear. The writer has found the latter method particularly well adapted to the testing of thermosetting plastics, without requiring any special testing jig if the ends are perfectly squared up. When good strength in excess of the material being bonded develops, there will be a compression and shear failure in the body of the material rather than in the glue line. The relative merit of three and two block test specimens has been the subject of a Forest Products Laboratory specification<sup>13</sup>, without any values obtained. Still other alternatives for test specimens have been suggested by Traux<sup>14</sup>. Butt and scarfed assemblies, when tested in flexure by a load applied at the center have demonstrated the efficacy of scarfed assemblies by the failure in the material rather than in the glue line, when scarfs above 10:1 have been reached.

The absence of numerous applications of organic plastics in cemented assemblies has no doubt precluded the development of standard testing specifications for their adhesives. Performance tests upon resin bonded and impregnated plywood, as in the manufacture of airplane propellers, are nevertheless significant. The plastics as well as the metals, however, are playing more important roles in the development of composite laminates and in structural assemblies, and it is quite probable that more detailed specifications will make their appearance.

*Army Air Force Specification No. 15065, "Panels, Impregnated Com-*

*pressed Wood*" (Phenolic Resin Impregnated Wood). This specification contains technical data bearing upon bonding problems. Shearing strengths perpendicular to laminations are specified as 7000 psi for rectangular specimens, and 5500 for cylindrical ones; shearing strengths parallel to laminations are 5000 psi for rectangular and 4500 for cylindrical specimens. These tests are upon impregnated woods rather than adhesives. The cementing of resin impregnated wood has attracted the attention of many laboratories inasmuch as a greater quantity of this material will be used in the post-war period. Both urea formaldehyde resin and phenol formaldehyde resin impregnated woods are the subject of current investigations as they offer bonding problems considerably different from straight unimpregnated woods.

### Tests for Paper and Leather Adhesives

Tests for paper and leather adhesives, with the possible exceptions of gummed tapes and labels which have attained large volume applications as specialty items, have been improvised by manufacturers of these materials. The stripping shear test where the flexible foil or paper is folded back upon itself and stripped from the surface under a constant load or constant rate of pulling is the most popular. Various manufacturers have established their own testing procedures for evaluating the effects of adhesives upon their own products. Some of the standard work along the line of adhesives for papers, leathers, foils, etc., are reflected in the following specifications:

*ASTM D-773 "Adhesiveness of Gummed Tape"*. This method covers the procedure for determining the adhesiveness of gummed tape not less than 2 inches in width, used for sealing shipping containers. The testing apparatus consists of the Hardnen-McLaurin gummed tape tester<sup>15</sup>. Kraft paper caliper 0.0074 to 0.008 inch and of 85 to 95 pounds weight basis is used. Relative humidity of  $50 \pm 2$  per cent is maintained. Two adjacent platens are so pivoted that the adjacent edges tilt upward and apart; the retardation of the swing of the platens by the gummed tape is recorded.

Wehmer describes various specialty adhesives and certain test methods which they require<sup>16</sup>—in particular the sealing of pressurized plane cabins. The method of test he points out will be determined by the manner in which the adhesive is to be used.

Davis discusses adhesive properties of flour, dextrin, water glass and other library pastes which are spread on manila paper and folded. This is repeated with successive dilutions of water until, after an hour assembly, the paste fails to hold<sup>17</sup>.

Adams describes an accelerated aging test for envelope adhesives at 60° for 72 hours<sup>18</sup>.

### Identification of Adhesives

With the developments of standard testing methods for adhesives there will be increasing interest in methods of identifying adhesives. Lehman has suggested the following<sup>19</sup>:

- (1) Starch and dextrin adhesives give the starch-iodine reaction.
- (2) Animal glues form a violet to red coloration in alkaline solutions of copper sulfate, and a precipitate with tannins.
- (3) Casein is characterized by its phosphorus content and by precipitation with rennet.

Rendle discusses identification of plywood glues by combining microscopic features and staining reactions with simple chemical and physical tests<sup>20</sup>. The thermosetting synthetics can usually be detected by their odor, especially when heated, while the thermoplastics can sometimes be determined by the solvents in which they are dissolved. More exact tests will be developed in time to aid in the identification and evaluation of adhesives.

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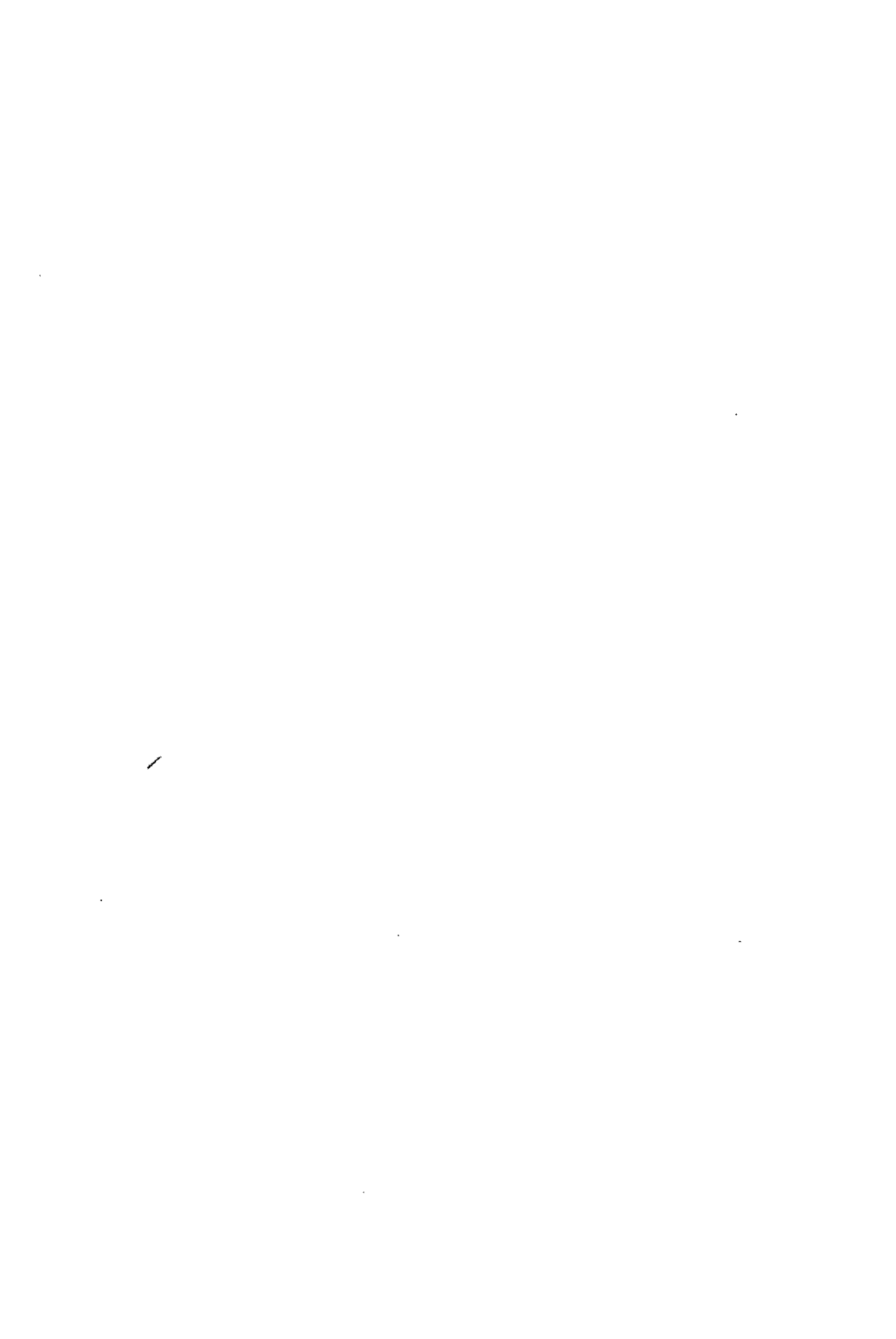
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